

**THE ROLE OF IRON COMPOUNDS ON THE STRUCTURE  
OF LATERITIC SOILS**

by

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## INTRODUCTION

Lateritic soils occur mostly in the tropics. They are derived from laterite ("red bricks") which (in the pedologic sense) would be defined as a parent soil material ranging from pure bauxite (or gibbsite rock  $\text{Al}_2\text{O}_3$ , 65%) to a material containing not less than 20% gibbsite or more than 5% Kaolins, with 3% hydrous  $\text{Fe}_2\text{O}_3$ , or with 30% of a mixture of Fe oxides, quartz, colloidal silica, and other accessory compounds. The material representing the lower end of this laterite range would thus have a combined silica content of about 25% and a total alumina content of about 33% (13% being free) gives a silica-alumina molecular ratio below 1.33 (16) which conforms with the standard suggested by Martin et al. (33).

With decreasing content of gibbsite and increasing content of Kaolin, the material might still be described as lateritic. These leached soils of the tropics do not show the general properties of silicate clays. They are not plastic, do not swell on wetting, are permeable, have a very low base exchange capacity, and are easy to cultivate when wet. They have a vivid red color, a high proportion of concretionary "stones" with a very low silica content (of which a small proportion is probably quartz), a low silica-alumina ratio in all fractions, especially in the clay. Martin et al. (33) examined a number of soils in Sierra Leone and found that the silica:alumina ratio varied from 1.05 to 2.11. They classified these as:

Silica / alumina ratios  $< 1.33$  should be called laterite and silica / alumina ratios 1.33 to 2.0 lateritic.

These soils differ from those in the temperate regions by the much higher content of kaolinite clay. Since they contain a high proportion of iron compounds, it is thought that iron compounds may play some role in the structure of these soils.

## REVIEW OF LITERATURE

### Nature of Iron Compounds in the Soil

Iron in soils can be divided into the following categories:

(a) The iron present in primary minerals, the nature of which will depend on the type of parent material undergoing weathering. Examples are: Ferromagnesium silicates (olivines, pyroxenes, and amphiboles), the biotite micas and the iron ores (hematite, ilmenite and magnetite).

(b) The iron present in secondary minerals, clay minerals containing iron as a structural element are the "hydromicas;" illites, nontronite, chlorites, vermiculite, chamosite, glauconite, griffithite, cronstedtite and greenatite (40).

The primary iron minerals in soils exist in the larger fractions, and separation of the clay fraction will serve to exclude most primary minerals, leaving the clay minerals, particularly illites and nontronite and the iron oxides, iron salts and iron associated with organic matter (collectively termed free iron).

Iron oxides usually constitute the bulk of the free iron, amounts of iron salts in soils being low except below pH's of about 5.5 (41). The occurrences of accumulations of free iron oxides in soils may be roughly divided into four categories:



(a) Iron concretions,

(b) Illuvial deposits in lower B horizons of podzolic soils,

(c) Laterite crusts,

(d) Iron oxides of agricultural soils and brown earths, which are not found as local concentrations owing to thorough mixing of the soils and general stable oxidative conditions.

Where iron concretions are absent both the total and free iron are concentrated in the  $< 2\mu$  clay fraction. In well drained soils the bulk of the iron oxides resides in the clay fraction which is more or less evenly distributed throughout the soil profile. In poorly drained soils the free iron is again associated with the clay fraction which tends to occur as accumulations in clay pans and illuvial horizons. This association of free iron oxides with clay minerals may be due to the adsorption of the oxides by clays.

The presence of large amounts of iron in the  $< 20\mu$  fraction is due to the formation of iron concretions or the cementing action of iron oxides, which is common in lateritic soils (31). The iron nodules or concretions appear to be formed by the presence of alternate oxidizing and reducing conditions suggesting that their precipitation is physico-chemical in nature. A second group of iron concretions owes their precipitation to biological processes. These are the iron concretions associated with root channels (4).

The following iron oxides are known to exist as definite compounds (40):

$\beta$   $\text{FeOOH}$ ---not yet recognized in nature  
 $\delta$   $\text{FeOOH}$

$\text{Fe}_3\text{O}_4$  magnetite - contains ferrous and ferric iron

$\alpha$   $\text{Fe}_2\text{O}_3$  hematite - red iron ore

$\gamma$   $\text{Fe}_2\text{O}_3$  - maghemite

$\alpha$   $\text{FeOOH}$  goethite - needle iron ore

$\gamma$   $\text{FeOOH}$  lepidocrocite

$\text{Fe}(\text{OH})_3\text{H}_2\text{O}$  - hydrated - ferric-oxide gel.

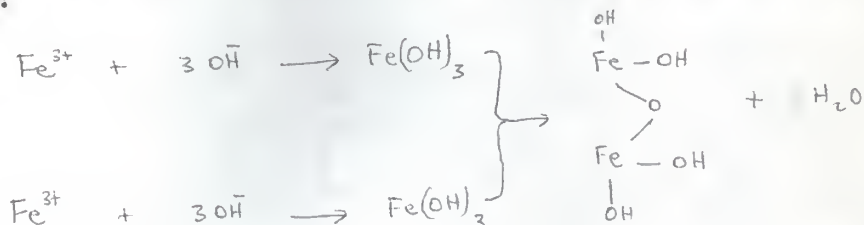
The most commonly occurring oxides are goethite and hematite. Generally hematite occurs in drier and more highly oxidized zones, usually nearer the surface, whereas goethite occurs more typically in wetter though well oxidized zones, often in subsurface horizons. Goethite is the predominant oxide in temperate regions.

Little is known about the conditions of formation of hydrated iron oxides in soils, but possible pathways of formation, as indicated by experimental work, show that the precipitation of iron from ionic solution can be brought about in two ways:

(a) by a rise in pH and

(b) by oxidation of ferrous iron in solution because the solubility product of ferric hydroxide  $10^{-38}$ , is much lower than that of ferrous hydroxide  $10^{-14}$ . A mixed hydroxide may also be produced, which has been given a solubility product of  $6 \times 10^{-18}$ .

A rapid precipitation of ferric iron, as is achieved by the addition of alkali to a solution of ferric ions, leads to a dark brown voluminous gel which ages slowly, the process being represented by the following scheme:



The resultant gel is usually given the formula  $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  and termed the "brown gel." The aging of this gel has been studied in detail and the products of aging appear to be goethite, hematite and hydrohematite or various mixtures of either two or three of these compounds. Formation of goethite and hematite appears to be the most feasible in tropical soils since goethite is formed by precipitation of ferric ions in solution at low pHs, and since all iron oxides transform to hematite when heated to a sufficiently high temperature. Kubiena (26) showed that tropical soils may be differentiated by micro-morphological differences in their content of a particular kind of  $\text{Fe}(\text{OH})_3$  or mineral. Thus preponderance of peptized amorphous  $\text{Fe}(\text{OH})_3$  indicate braunlehm and flocculated amorphous  $\text{Fe}(\text{OH})_3$  indicates an earthy braunlehm, pseudogleys contain mottles of peptized amorphous  $\text{Fe}(\text{OH})_3$  and crystallized aggregates of goethite and lepidocrocite in a more or less Fe-free matrix of light color. Fine crystals of goethite and hematite in the matrix indicate rotlehm, their flocculation indicates roterde and their formation into coarse



aggregate-complexes (also of maghemite and magnetite) indicates laterite. In this discussion of the effect of iron compounds on the structure of lateritic soils, particular attention should be placed on iron oxides, which constitute the bulk of the free iron, amounts of iron salts in soils being low except below pHs of about 5.5. The diagram below shows the interrelationships between the iron oxides and some closely related compounds (Fig. 1) (40).

On the consideration of ferrous iron in the soil, Ignatieff showed that soil must be water logged a considerable period of time before iron moves in the ferrous state, and that certain soils, at least, can hold a considerable amount of iron in the divalent form which is not easily removed by water, but can be extracted by  $\text{AlCl}_3$  solution. The presence of organic matter under anaerobic conditions encourages formation of ferrous iron (20). It has also been demonstrated that aluminum and ferric salts treatments reduce the base exchange capacity of soils (42). If only small or moderate amounts of ferric and aluminum salts are used, all of the base exchange capacity will not be destroyed. Ferrous salts are found to be readily exchangeable for calcium in soils.

#### Chemical Composition of Lateritic Soils

Before a thorough discussion on the structure of lateritic soils is achieved one must first consider the chemical composition of this type of soil. Maud (38) working on laterite and lateritic soils in coastal Natal, South Africa, gave the following chemical composition of the lateritic soil, Tables 1 to 4.



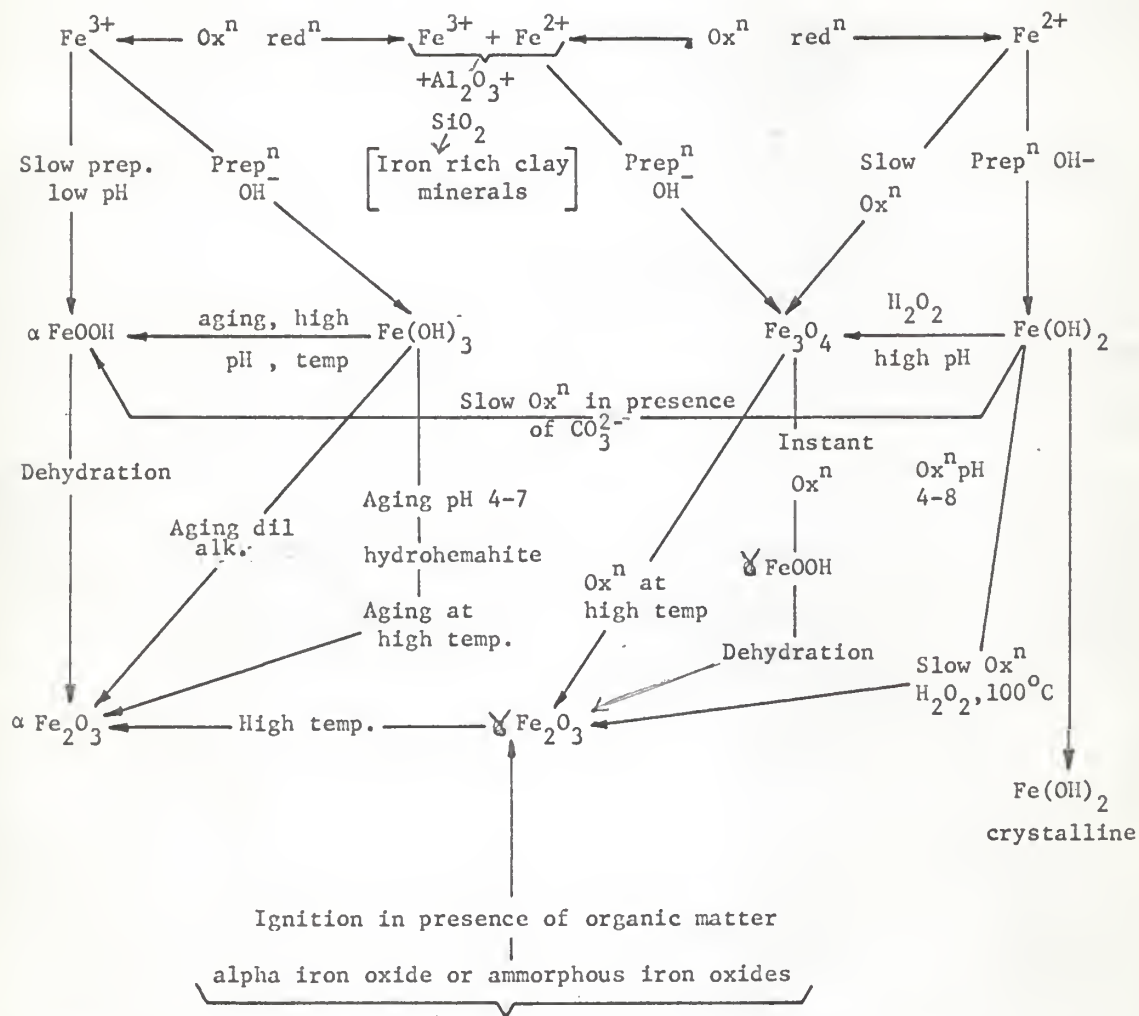


Fig. 1. Interrelationships between the iron oxides and some closely related compounds

Table 1. Exchangeable cations in Indi-Inanda profile.

Horizon in inches	pH 1:25 soil:H <sub>2</sub> O	Exchangeable cations <sup>a</sup>					Total C.E.C.	Saturation
		H	Ca	Mg	K	Na		
		m.e./100 g.						
0 - 21	5.7	8.87	0.25	0.20	0.13	0.27	9.72	8.7
21 - 35	5.6	9.34	0.85	0.75	0.13	0.23	11.30	17.2
35 - 56	5.5	9.34	1.50	0.50	0.12	0.25	11.71	20.2
56 - 68	5.0	8.20	0.75	0.20	0.12	0.23	9.50	13.7
68 - 80	5.2	1.33	0.50	0.20	0.10	0.15	2.28	41.7
80 - 92	4.8	3.34	0.50	2.25	0.10	0.38	6.57	49.2

<sup>a</sup>Determined in N ammonium acetate, pH 7.0.

Table 2. Chemical composition of the clay fraction.

Depth of Horizon inches	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO
0 - 8	31.48	20.48	45.52	2.30	0.48	0.02
8 - 20	30.20	21.76	44.60	2.35	0.49	Trace
20 - 43	29.68	22.08	45.13	2.00	0.39	Trace
43 - 64	32.64	21.44	43.02	1.96	0.38	Trace
64 - 72	34.12	19.52	39.32	1.70	0.66	Trace
Average	31.32	21.38	43.82	2.05	0.44	Trace

Table 3. Derived data on the clay fraction.

Horizon in inches	$\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$
	molar ratios			
0 - 8	4.09	1.17	0.91	0.29
8 - 20	3.70	1.15	0.88	0.31
20 - 43	3.57	1.11	0.85	0.31
43 - 64	4.05	1.29	0.98	0.32
64 - 72	4.65	1.47	1.12	0.31
Average	3.89	1.21	0.92	0.31

Table 4. Minerals in Inanda profile.

Horizon in inches	Kaolinite	Illite	Montmorillonite	Gibbsite
0 - 21	Practically	Amorphous	----	W
21 - 35	t	"	----	W
35 - 56	--	"	----	VW
56 - 68	t	"	----	W
68 - 80	t	"	----	W
80 - 92	MW	---	----	W

MW - medium weak intensity line

W - weak

VW - very weak

t - trace

These data confirm the kaolinitic nature of the soil as well as indicating the presence of hydrated oxides of iron and aluminum. The pH of the laterite-derived surface soil throughout coastal Natal varies between 4.5 and 5.5. Organic matter averages 7.2 per cent with 4.19 per cent carbon and 0.24 per cent nitrogen. The exchangeable base status of the soil is very low. X-ray diffraction determination of the clay minerals in the Inanda soil profile indicated that the profile is nearly amorphous throughout, and it is only in the bottom horizon that the minerals may be determined with any degree of certainty. The presence of gibbsite and kaolinite was also confirmed by differential thermal analysis.

Joffe (22) pointed out that Stremme was among the first to propose that Fe and Al compounds move through the soil in the form of colloidal hydroxides. Soils consist of colloids (Al silica gels, silicic acid, iron, aluminum, and humus) lying alongside some crystalloidal substances.

Aluminum and Fe are the two outstanding trivalent cations widely distributed in soils. Their content in the earth's crust is 7.8 per cent and 5.46 per cent respectively. From a study of the anion effect and reaction of the dispersed medium on the condition of state of iron and aluminum in soils, it is clear that as far as the inorganic compounds of iron and aluminum are concerned the molecular state of either one of these two cations rarely persist in the soil. It is very likely that within the sphere of "local action" in close proximity of the roots or around centers of active nitrification soluble iron and aluminum do exist temporarily (23). Colloidal iron and aluminum



sols of various degrees of dispersion may exist, especially in the presence of the nitrate anion and at moments of the relative absence of the sulphate and phosphate anions. The bulk of the iron and aluminum split off from the mineral complexes in the process of weathering exist in the soil as a gel, and, as such, are distributed throughout the soil profile. The iron and aluminum going into solution do not represent the total quantity of gel present in the soil. It proves, however, the point that iron and aluminum do exist in the gel state.

The different soil colloidal materials vary widely in alterability. Some soil colloids are markedly altered in properties, whereas those of other soil colloids are not appreciably affected by the substitution of any cation. The ranges of alteration of different soil colloids correlate fairly well with magnitudes of the properties of the untreated or Ca saturated material, with the total content of exchangeable bases, and with the silica-sesquioxide ratio of the colloids (1). Anderson and Byer (2) indicated that there is a correlation between the silica-sesquioxide ratio of the colloids and certain physical properties in soils. Thus working with various colloids from a standpoint of (a) the chemical composition, (b) their saturation capacity for bases, (c) the effect of different exchangeable cations on (i) their state of flocculation or dispersion as related to charge and hydration, (ii) their relative degree of hydration as indicated by viscosity and swelling measurements, (iii) their permeability to water, they found that there is a correlation between the silica-sesquioxide ratios and certain physico-chemical properties of the colloids.

Data in Table 5 show that Davidson is a lateritic soil if a

Table 5. The chemical composition of the colloids extracted from the Iredell, Davidson, and Putnam soils.

Constituent	Iredell			Davidson			Putnam
	A	B	C	A	B	C	B
	%						
SiO <sub>2</sub>	38.12	40.81	39.72	33.87	36.44	33.80	50.22
Al <sub>2</sub> O <sub>3</sub>	26.65	27.83	27.34	32.77	30.14	29.56	27.65
Fe <sub>2</sub> O <sub>3</sub>	19.20	17.26	17.31	16.39	20.40	23.65	4.74
MnO	0.16	0.02	0.01	0.51	0.28	0.08	0.011
CaO	0.83	0.71	0.77	0.50	0.52	0.34	0.92
MgO	1.03	0.99	0.82	0.93	0.64	0.56	1.52
K <sub>2</sub> O	0.17	0.16	0.17	0.27	0.05	0.19	0.85
Na <sub>2</sub> O	0.06	0.03	0.07	0.18	0.20	0.08	0.449
TiO <sub>2</sub>	0.85	0.76	0.69	0.71	0.64	1.01	--
P <sub>2</sub> O <sub>5</sub>	0.64	0.58	0.36	0.27	0.25	0.45	--
Volatile matter	12.64	12.27	12.80	15.40	13.02	12.85	13.37
	Molar Ratios						
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.43	2.49	2.46	1.76	2.05	1.95	3.08
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>	1.66	1.78	1.76	1.30	1.44	1.28	3.02
	Percentage						
Saturation capacity of colloid	--	35	--	--	12	--	60

$\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$  molar ratio of 2 or less as suggested by Harrassowitz is used as the criterion for lateritization. The decrease in the  $\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$  ratio from Putnam to the Davidson is accompanied by a decrease in the total cation exchange capacity of the complex from 60 to 12 me/100 g colloid. The magnitude of the charge on the particles has also been shown to decrease with the silica-sesquioxide ratio, since the intensity of the charge of the colloidal particles is considered as one of the main factors influencing the stability of colloidal suspensions, soils with low silica-sesquioxide ratio such as the Davidson should be expected to flocculate. The content of exchangeable bases of colloids parallel the silica-sesquioxide ration (34, 3).

Difference between bauxite, laterite and lateritic soils is shown in Table 6. In order to facilitate comparison of the colloids of the different classes, their major constituents (Table 6) have been recalculated on the basis  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = 100$ . These values, together with the silica-sesquioxide ratios from the previous table and similar results from Amarillo series (chernozem from Texas), superior (Podzol from Wisconsin) and Beckett (Podzol from Massachusetts), are presented in Table 7.

In comparing the usual silica-sesquioxide ratio with exchange capacity in the 23 cases, Wadsworth (52) obtained a correlation coefficient of  $+0.855 \pm 0.038$ . If the simpler silica-alumina ratio is used, the correlation coefficient increased to  $+0.876 \pm 0.033$ . Computing the ratio once more as sesquioxide-alumina ratio reduces the correlation coefficient to  $+0.574 \pm 0.094$ . If significance can be claimed for these differences in the correlation coefficients, there seems to be some evidence that  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  differ widely in their base exchange characteristics, whereas  $\text{Fe}_2\text{O}_3$  is relatively inert. Assuming that the



Table 6. Chemical composition of laterite colloids of Davidson and Nipe soils and bauxite (as recorded by Anderson, M. S. and Myers, H. G.), Davidson clay loam from North Carolina, Nipe near Preston, Cuba, and Bauxite from Arkansas (2).

Pro- file No.	Soil Series	Depth	Hori- zon	%												Mols.	
				SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Igni- tion loss	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
in.																	
4	Davidson	0 - 9	A	34.43	32.10	12.40	0.24	0.58	0.92	0.50	0.03	0.99	0.25	0.17	17.08	1.46	
		9 - 36	B <sub>1</sub>	36.92	31.67	16.03	.06	.56	0.41	.37	none	0.92	0.18	0.12	13.14	1.49	
		36 - 60	B <sub>2</sub>	35.37	29.44	20.61	.08	.35	0.36	.18	Tr.	0.98	0.17	0.11	12.30	1.42	
		60+	C	35.24	29.69	20.10	.30	.50	0.06	.17	Tr.	.95	0.36	0.14	12.53	1.40	
(Lateritic)																	
5	Nipe	0 - 12	1	10.19	15.84	62.51	--	.23	0.05	--	Tr.	--	--	--	9.86	.31	
		40 - 60	2	5.55	11.47	66.59	.36	--	0.07	.07	0.02	0.41	0.03	0.14	13.51	.17	
		100 - 144	3	12.89	17.93	53.52	.58	--	0.21	.16	0.03	0.57	0.05	0.14	12.70	.42	
(Laterite)																	
6	Bauxite	156 - 214	4	23.83	43.29	7.56	.35	--	0.09	.02	0.08	4.44	0.23	0.15	19.70	.84	
		250 - 290	6	44.02	39.42	1.83	.10	--	0.06	.05	--	0.37	0.03	0.05	13.93	1.84	



Table 7. Chemical composition of soil colloids calculated on the basis  
 $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = 100$ .

Profile No.	Soil Series	Depth	Horizon	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	Mols $\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$
							%
1	Amarillo	0 - 5	1	62.09	27.09	10.82	3.10
		10 - 20	2	62.19	27.42	10.39	3.09
		30 - 40	3	62.43	27.28	10.29	3.13
		54 - 64	4	61.35	28.53	9.81	2.97
		70 - 75	5	62.20	28.56	9.24	3.06
		96 -100	6	62.97	27.57	9.46	3.18
2	Superior	0 - 3	A <sub>0</sub>	66.44	23.89	9.67	3.76
		3 - 8	A <sub>1</sub>	68.52	24.72	6.75	4.01
		12 - 30	B	45.01	35.81	19.18	1.59
		30 - 40	C	55.14	28.77	16.09	2.40
3	Beckett	0 - 6	A <sub>0</sub>	52.35	29.64	18.01	2.16
		6 - 11	A <sub>1</sub>	59.80	31.56	8.64	2.74
		11 - 13	B <sub>1</sub>	28.03	25.15	46.82	.86
		13 - 24	B <sub>2</sub>	39.46	36.71	23.83	1.28
		24 - 36	C	46.71	37.50	15.79	1.67
4	Davidson	0 - 9	A	43.62	40.67	15.71	1.46
		9 - 36	B <sub>1</sub>	43.63	37.43	18.94	1.49
		36 - 60	B <sub>2</sub>	41.41	34.46	24.13	1.42
		60 +	C	41.44	34.92	23.64	1.40
5	Nipe	0 - 12	1	11.51	17.89	70.60	.31
		40 - 60	2	6.64	13.72	79.64	.17
		100 -144	3	15.28	21.26	63.46	.42
6	Bauxite	156 -214	4	31.91	57.97	10.12	.84
		250 -290	6	51.62	46.23	2.15	1.84

materials exist in simple uncombined forms, we may write:

$$\begin{aligned} \text{Base exchange capacity} = & x \text{ per cent SiO}_2 + y \text{ per cent Al}_2\text{O}_3 \\ & + z \text{ per cent Fe}_2\text{O}_3 + w \text{ per cent organic.} \end{aligned}$$

where

$x = +0.01570$  = exchangeable base (m.e. per gram  $\text{SiO}_2$ )

$y = -0.01044$  = exchangeable base (m.e. per gram  $\text{Al}_2\text{O}_3$ )

$z = +0.00033$  = exchangeable base (m.e. per gram  $\text{Fe}_2\text{O}_3$ )

$w = +0.00911$  = exchangeable base (m.e. per gram organic matter)

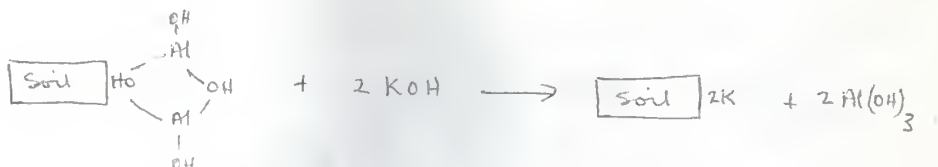
when these values were substituted in the equation above a correlation coefficient of  $+0.919 \pm 0.025$  was obtained.

Significant as this relation seems to be, it is based upon values which are rather unexpected. The positive values for  $x$ ,  $w$ , and  $z$  indicate that  $\text{SiO}_2$ , organic matter, and  $\text{Fe}_2\text{O}_3$  possess base exchange capacities in the order named. The negative value for  $\text{Al}_2\text{O}_3$  suggests that this material not only fails to possess base exchange capacity but actually tends to depress that characteristic in material adjacent to it. If the negative sign for  $\text{Al}_2\text{O}_3$  may be accepted, it would be reasonable to suppose that this material is particularly or exclusively active in anion adsorption. In fact, Mattson attacking the problem from an entirely different angle, reports that "with an increase in the silica content of the colloid we find an increase in the cation adsorption and a decrease in anion adsorption." And again, "as the silica-sesquioxide ratio increases, the colloids assume a more pronounced electronegative character. . ."

From the evidence available, there seems to be no reason for belief that  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  exist in soil colloids in any form

other than the simple oxides or hydrated oxides. The base exchange capacity of colloids seems to be a function of their chemical composition as well.  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and organic matter appear to adsorb these cations, whereas alumina seems to repel cations and possibly adsorbs anions. Toth (51) in his study of the anion adsorption by soil colloids in relation to changes in the iron oxides, showed that the hydrated oxides of iron and aluminum do not possess an appreciable cation exchange capacity but do retain certain anions, especially the phosphates and silicates, over a wide range of pH. The adsorption of anions by the oxide gels, which can function as acidoids, imparts new properties to the gel.

Mattson (35) showed that lateritic soils consist of soil colloidal material with a low silica-sesquioxide ratio below 2 and which usually have a reddish or yellow color. Such materials, from all indications, contain free sesquioxides. The aged gel of these oxides is not very dispersible and is chemically rather inert. Clark (11) showed that soils containing free oxides of iron and aluminum have low CEC when neutral salts were used for exchange saturation but to have higher values if the measurements were made with solutions buffered at pH 7. The pH dependent nature of the exchange capacity of the soils was attributed to the fixation of Al and Fe by the silicate clay and possibly by the organic matter. The conversion of the fixed Al and Fe to  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  was used to explain the higher C.E.C. values obtained at higher pH values and the slow extended release of hydrogen by the soils.



The lower solubility of  $\text{Fe}(\text{OH})_3$  than  $\text{Al}(\text{OH})_3$  probably accounts for the observation that, at pH 5.5, Fe was not fixed as extensively by silicate clays as was Al. At lower pH values it is conceivable that more extensive fixation of Fe might have occurred. The exchange sites occupied by fixed iron and aluminum cannot be considered as "exchange acidity" and exchange sites occupied by these fixed constituents should not be considered when estimating the percentage base saturation of a soil, because, the fixed aluminum and iron are bonded to the clays (and of course organic exchange material) by specific mechanisms, and for this reason cannot be replaced to any extent by solutions of strong electrolytes.

#### Anion Adsorption by Fe and Al

Microbiological consumption, chemical precipitation and physico-chemical adsorption are responsible for phosphate fixation in soils. The amount of phosphate consumed by soil microorganisms is relatively small, most of the fixation being the result of precipitation and adsorption. Iron and aluminum serve as precipitating agents at pH values below 5.5. Calcium plays a dominant role at pH 6.5 and Mg enters the picture at 7.5. But precipitation by these ions is

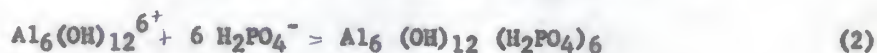


inadequate to explain the high phosphate fixation which normally occurs. In soils of such high fixing capacity, most of the phosphate is colloid-bound or saloid-bound, the colloid-bound phosphate being replaceable by hydroxyl, humate and silicate ions, and the saloid-bound phosphate by sulphate, chloride, citrate, and tartrate ions. The phosphate fixing capacity of soil colloids is closely related to their silica-sesquioxide ratios. Under conditions of low pH, soils having a low ratio (containing large amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) fix more phosphate than those having a high ratio. Under conditions of high pH the reverse may be true, because those having a high silica: sesquioxide ratios also have a high CEC and the exchangeable calcium functions as a fixing agent. Yellow soils have a greater fixing power than red soils containing the same amounts of  $\text{Fe}_2\text{O}_3$ , because of the greater degree of hydration of their oxides (6).

The mechanism of phosphate fixation was described as either precipitation or adsorption (17). Precipitation refers to a process in which phosphate precipitates as difficultly soluble compounds with iron and aluminum in acid soils or with Ca in neutral or alkali soils. Low and Black (29) hypothesized that kaolinite dissociates into aluminum and silicate ions in accordance with solubility product principles, and that phosphate precipitates the aluminum, thereby disturbing the equilibrium and causing more clay to dissolve. Kittrick and Jackson, as quoted by Hsu et al. (19), suggested that adsorption and precipitation result from the same type of chemical force. The approach was later elaborated by Hsu and Rennie (19) in their study on the reaction

between phosphate and amorphous aluminum hydroxide. Hsu pointed out that whether this process is precipitation or adsorption is dependent on the size of the polymer, which is in turn dependent on pH and the solution phosphate concentration.

In a moderately acidic medium (such as pH 4) with a high phosphate concentration, the reaction process may be a typical precipitation following equations (1) and (2).



In a slightly acid to neutral solution (pH 6 to 7) of a dilute phosphate solution, amorphous aluminum hydroxides (that is, high hydroxyl aluminum polymers of very high hydroxyl ion content) are stable and phosphate is adsorbed on the surface. The comparison of the products resulting from these two processes is illustrated in Fig. 2.

The diagrams illustrating the similarity between the processes of precipitation and adsorption (X = phosphate ions), Fig. 2 (a) represents phosphate precipitated as  $\text{Al}_6 (\text{OH})_{12} (\text{H}_2\text{PO}_4)_6$ , or  $\text{Al} (\text{OH})_2 \text{H}_2\text{PO}_4$  and (b) represents phosphate adsorbed by amorphous aluminum hydroxide. These two processes, however, may not be distinguishable when aluminum is present in some species of intermediate size such as  $[\text{Al}_{32} (\text{OH})_{52}]^{44+}$  and  $[\text{Al}_{54} (\text{OH})_{144}]^{18+}$ .

Hsu (18) suggested that when acidic soil was aged in a dilute phosphate solution for one year, fresh ferric hydroxide formed as a

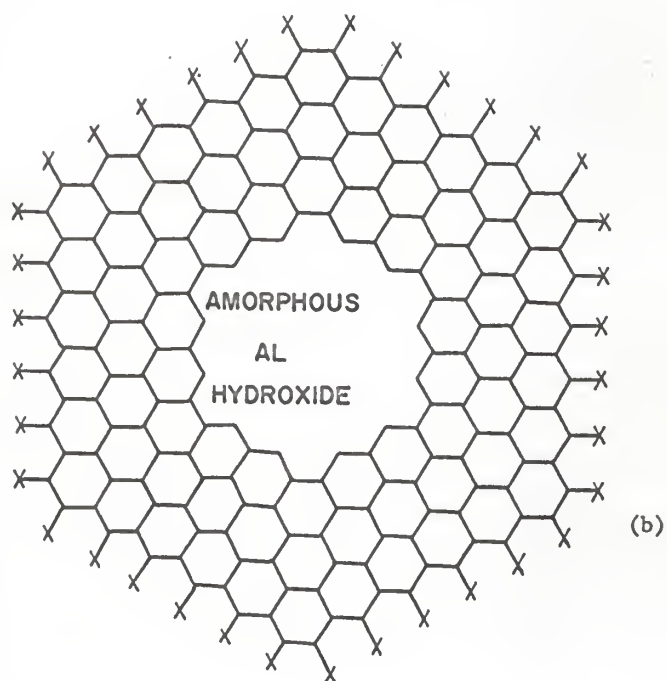
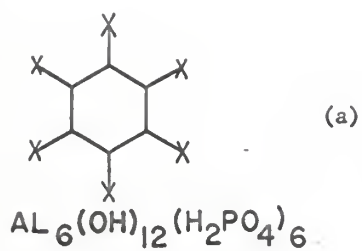


Fig. 2. Diagram showing the similarity between precipitation and adsorption of phosphate by aluminum hydroxide.

separate phase, which retained most of the phosphate removed from the solution. The retention of phosphate on the iron oxide ring is accompanied by a decrease in the native aluminum and iron-bound phosphate in soil. The molar ratio of Fe/P of the iron oxide ring is about 18:1.

Hsu (18) also suggested a process of phosphate fixation due to isomorphous substitution, in which precipitation occurs when phosphate removes Al (or Fe) completely from the lattice and precipitates as a new phase. Adsorption occurs when phosphate can break only part of the Si-O-Al or Al-OH linkages, leaving Al or Fe still in the lattice. In a strongly acid medium, the phosphate will first be adsorbed by the hydroxides, and oxides but will later be gradually transformed during aging into  $M(OH)_2H_2PO_4$ -type of compound. Broomfield (8) also supported the idea of phosphate sorption by acid soils, which is largely due to various forms of active iron and aluminum in the soil. This anion effect on the Fe and Al colloids tends to decrease their degree of dispersion and thus decrease the coefficient of diffusion. However the Fe colloids decrease their degree of dispersion at much longer ranges of hydrogen ion concentration than the aluminum, and this would impede the diffusion of the Fe (23). Larsen et al. (27) supported the idea that for noncalcareous mineral soils, the formation of nonlabile phosphate at a rate controlled by hydrogen-ion concentration is responsible for the fixation of the applied phosphate.

It has been proved that sulphates are also adsorbed by iron and aluminum oxides (28). Mattson (36) postulated that the adsorption of the anions increases with the valence of the ion and with the sesquioxide



content of the soil materials. He also showed that only soil materials with high sesquioxides content and which have a reddish or yellowish color become electropositive in hydrochloric acid solutions and adsorb appreciable quantities of this acid. This behavior is due to the presence of free sesquioxide which combines with the acid forming insoluble basic salts which dissociate the anions forming an electro-negative outer Helmholtz layer. The removal of sesquioxides from soil colloidal materials prevents the adsorption of sulphate and chloride ions. Ensminger (15) showed that the sub-surface layers usually contain more sulphate and are more capable of adsorbing more sulphate from solution than the surface layer. The mechanism of sulphate adsorption in soils has been studied only to a very limited extent. Aluminum hydroxide retains six times as much sulphate as iron hydroxide at the isoelectric point. It has been found that as the pH is raised from acid to neutral, the amount of sulphates adsorbed is reduced. Increasing the phosphate concentration in the soil has been found to decrease sulphate adsorption. Kamprath et al. (24) found that sulphate ions were retained more strongly than chloride ions, but less strongly than phosphate. The effect of pH on the adsorption of sulphate is presented in Fig. 3.

The effect of various proportions of sulphate and phosphate on the retention of sulphate and phosphate by a Nipe soil and a H-Al-bentonite is presented graphically in Fig. 4.

Lutz (32) studied the effects of adsorbed chloride and ferric ions by clays and arrived at the conclusion that an increase in

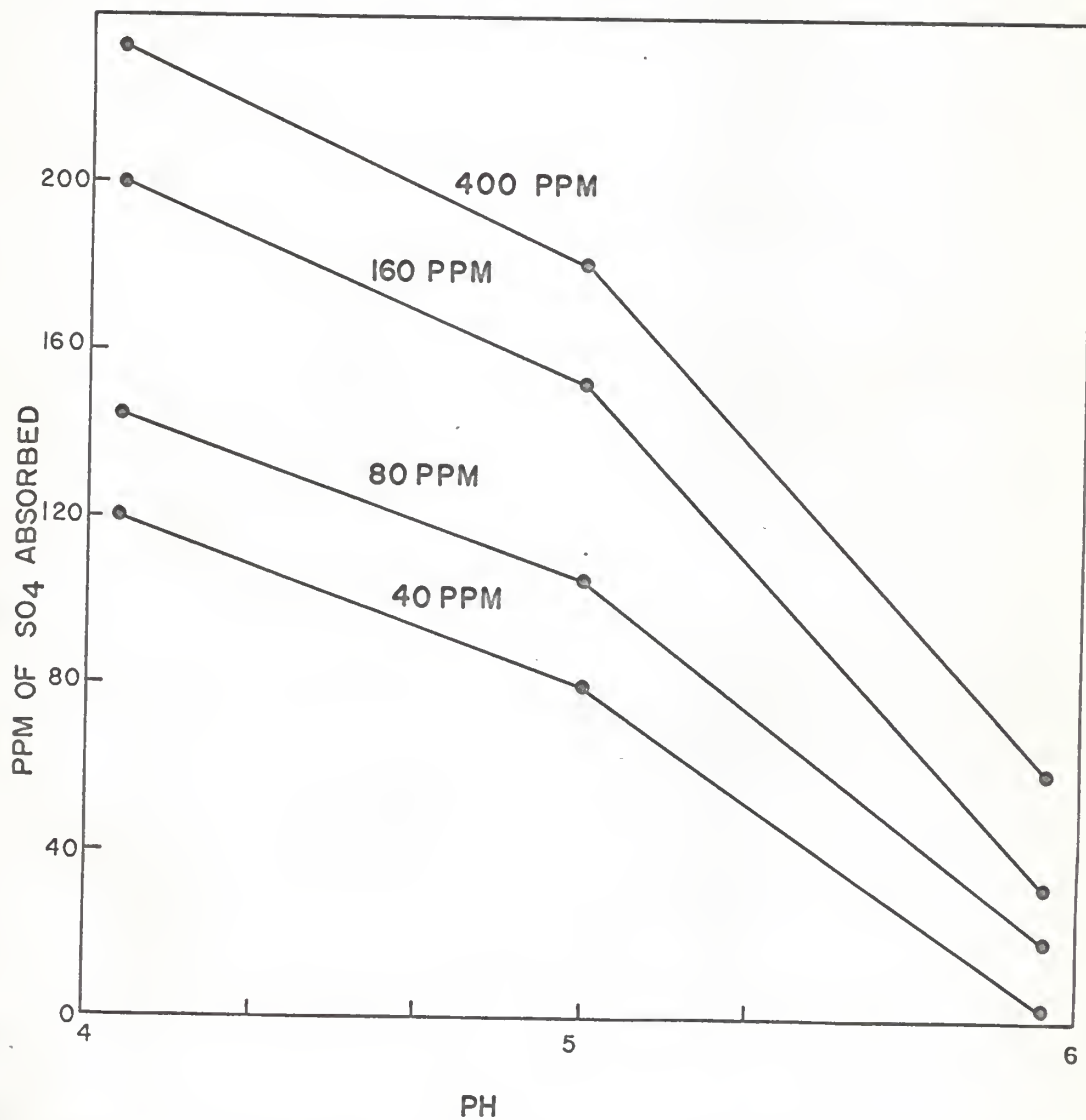


Fig. 3. Effect of pH on the adsorption of sulphate by a Cecil soil at various solution concentrations of sulphate (24).

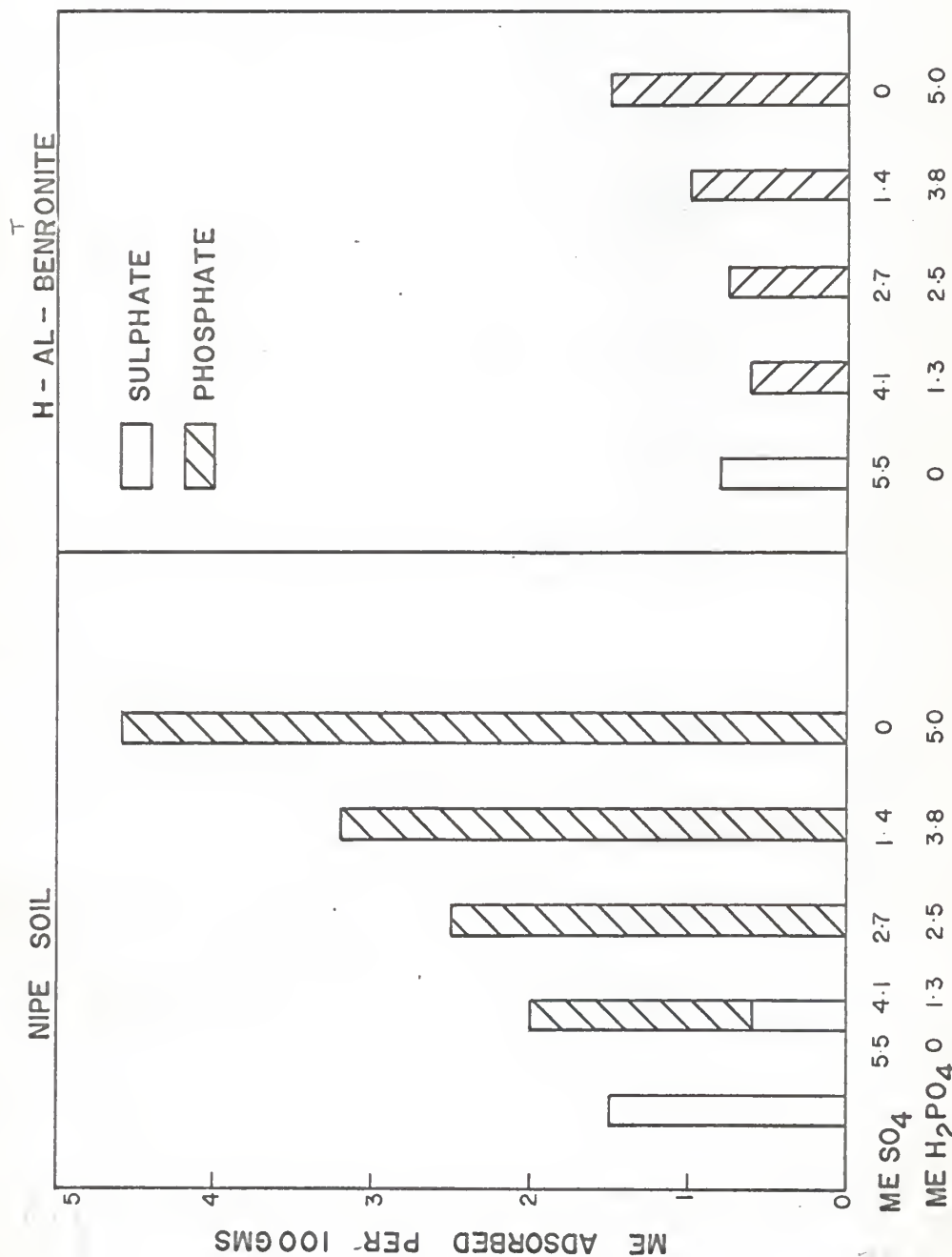
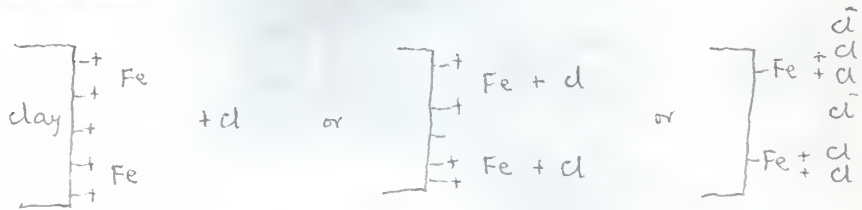
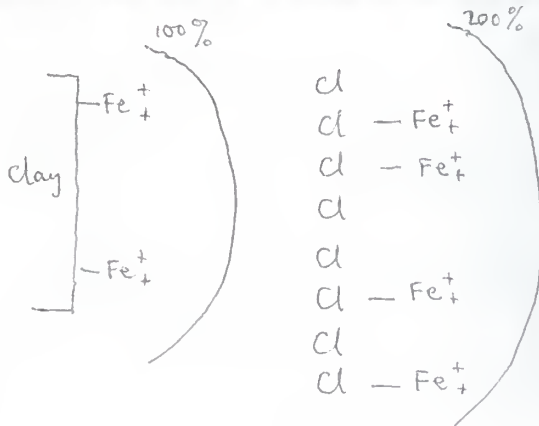


Fig. 4. The effect of various proportions of sulphate and phosphate on retention of sulphate and phosphate by a Nipe and a H-Al-Bentonite soil.

adsorption of Fe was associated with an increase in chloride ion adsorption but not as a linear function, as shown by Fig. 5. He used a bentonite suspension, which adsorbed iron from the smaller additions with a majority of the  $\text{Fe}^{++}$  valencies being held by the clay and a small part of them available to adsorb Cl. This is pictured as follows:



At saturation the  $\text{Fe}^{+++}$  is the inner layer and Cl is adsorbed as the outer. Above 100 per cent saturation with Fe the Cl becomes the inner layer and Fe is adsorbed as the outer.





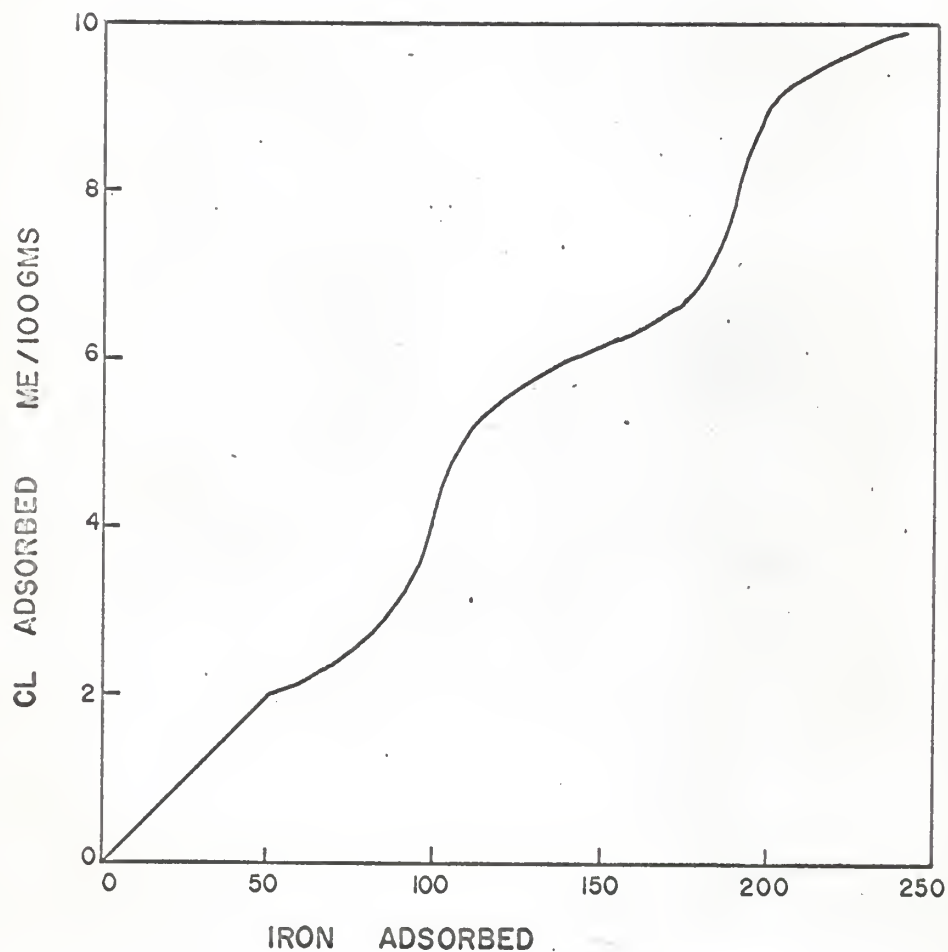


Fig. 5. The effect of iron adsorbed on the adsorption of chloride ion.

The swelling of the dried colloid and hydration of the suspended colloid were more nearly proportional to the Cl/Fe ratio than to the total Fe content. Low Cl/Fe ratios were associated with low hydration and small amounts of swelling. Thus, the proportion of Fe to anion and, perhaps the kind of anion, are important influences on the swelling and hydration of bentonite. The low swelling and hydration caused by the Fe is in agreement with the observations and experimental data on lateritic soils. The hydration and swelling and the  $\text{Cl}^-$  adsorption data indicate that Fe is probably a very important factor influencing certain physico-chemical properties of lateritic soils, Fig. 6.

Mattson Sante (37) showed that the displacing power of various anions involved in anion adsorption by Fe and Al could be represented as follows:



#### Organo-Metallic Interactions in Soils

Organic matter in the soil can form stable combinations with metal ions and hydrous oxides. The formation of a complex can be represented by the equation:



where

A is the metal ion and

B the ligand.

With the aid of known molecular weight of the organic matter the weight ratios at which metals and organic matter combined were expressed in

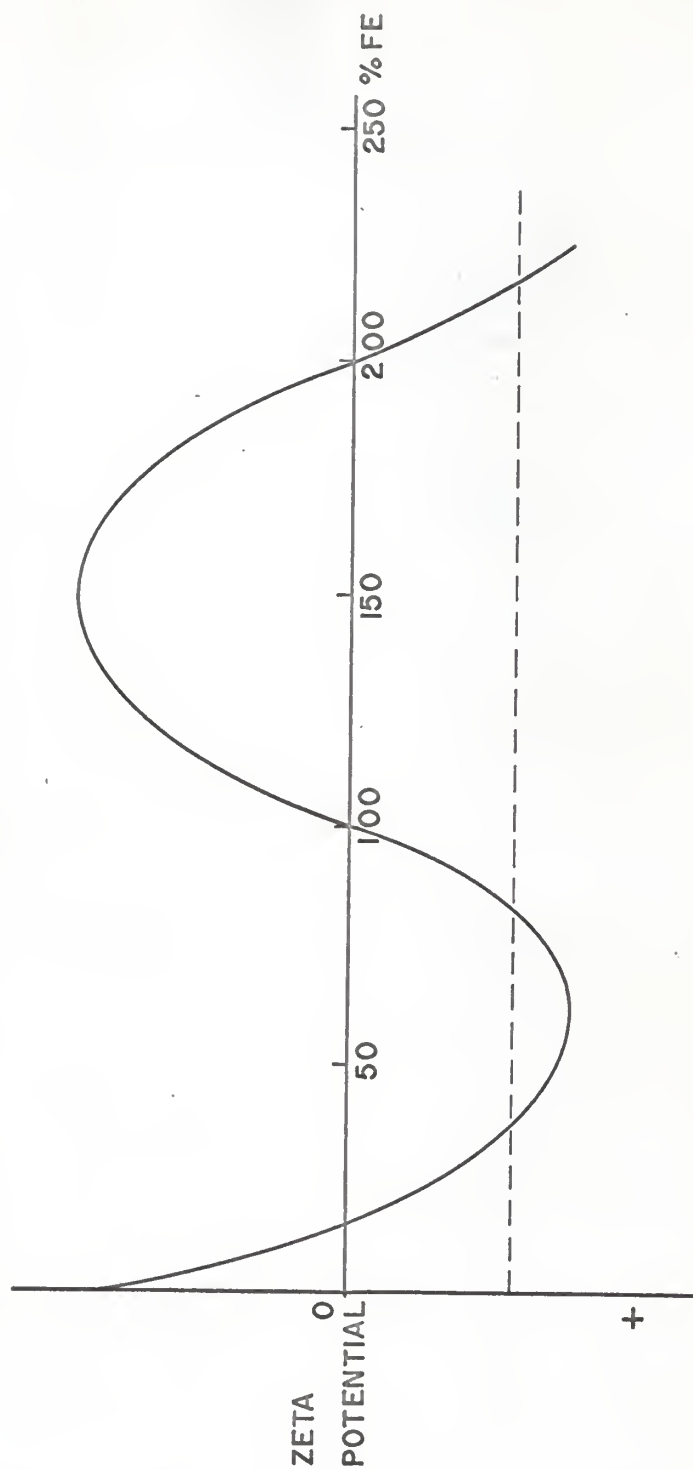


Fig. 6. The effect of adsorbed Fe on the physico-chemical properties of lateritic soils (32).

terms of molar ratios. While ferric iron, aluminum and copper formed water-soluble 1:1 molar complexes with organic matter at approximately pH3, 2:1 molar water-soluble complexes were formed at pH5 between iron ( $\text{Fe}^{+++}$ ), copper, calcium and organic matter. Schnitzer et al. (46) further showed that indications were also obtained of the formation of water-insoluble 6:1 molar complexes between ferric iron, aluminum and organic matter, involving in each instance one carboxyl group per atom of metal. These suggest the formation of a range of molar complexes, varying from 1:1 to 6:1 and becoming increasingly water-insoluble as more metal is complexed. Schnitzer suggested the formation of electrovalent bonds between negatively charged carboxyl groups of the organic matter and positively charged partially hydroxylated iron and aluminum compounds.  $\text{Fe}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_2^+$  at pH ranges between 3 and 8, which can be rationalized by writing the following simplified equation, taking  $\text{FeOM}$  as an example.



(R denotes the organic matter molecule without the six carboxyl groups).

The important role of the carboxyl groups in the organo-metallic reactions, was demonstrated by blocking the acidic groups by methylation. Data (Table 8) showed that, as more and more of the acidic groups were blocked, the amounts of iron taken up decreased (47). The iron uptake by methylated OM-II at pH 3 was practically zero. The compositions of the complexes ranged from 1:1 to 6:1 molar (metal:OM) and as more metal was complexed the complexes became increasingly water-insoluble. Evidence was also presented for the formation of



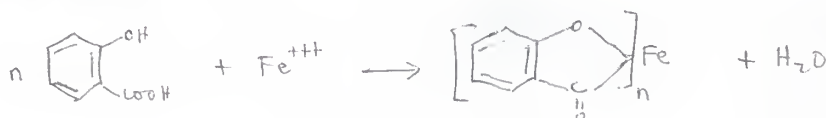
Table 8. Iron uptake by untreated and methylated OM.

pH	Untreated OM	Methylated OM <sup>*</sup>	
		I	II
	mg Fe/g OM		
pH 3	16.39	11.55	0.06
pH 5	22.37	10.88	1.96
	mmoles Fe/mole OM		
pH 3	196.92	146.82	0.84
pH 5	268.84	128.33	27.44

\*The two methylated samples are referred to as Methylated OM-I and Methylated OM-II. Methylated OM-I refers to OM methylated once and Methylated OM-II refers to OM methylated twice.

metal-carboxylate bonds, involving in each instance at least one carboxyl group per metal ion. Schnitzer (48) further showed that iron in the lower complexes occurred as  $\text{Fe}(\text{OH})^{++}$  and in the higher complex as  $\text{Fe}(\text{OH})_2^+$ . Aluminum appeared to be present in the low complex as  $\text{Al}(\text{OH})^{++}$  and as  $\text{Al}(\text{OH})_2^+$  in the high complex.

Schnitzer (49) gave the order of metal retention by the organic matter at pH 3.5 as  $\text{Fe} > \text{Al} > \text{Cu}$ , at pH 5.0 as  $\text{Fe} > \text{Al} = \text{Cu}$ . It was also found that blocking of either acidic carboxyls or phenolic hydroxyls caused significant reductions in metal retention. Both groups appeared to react simultaneously as that known to occur between ferric iron and salicylic acid:



where  $n$  can vary from 1 to 3 and the charge on the chelate from 1 to -2.

### Effect of Iron on Soil Aggregation

As Russell (45) pointed out, flocculation is the cause of a stable crumb structure. The process of flocculation is generally pictured as the separation of a dispersed phase, in the form of flocs, from a dispersion medium. Crumbs formed by drying a soil paste are harder if the paste is deflocculated than if it is flocculated, whether the cause of flocculation is the presence of an electrolyte or of exchange cations such as aluminum which prevent the paste from being deflocculated. Flocculation of the original soil paste is a sufficient, though not a necessary condition that the crumbs formed by drying the paste shall be water-stable. Colloidal material must be present in a soil for it to be able to form crumbs.

Russell pointed out that clay could only form crumbs if 5 conditions were fulfilled, namely:

(a) A certain proportion of the clay particles must be smaller than  $1\mu$  and probably smaller than  $1/2\mu$  in diameter.

(b) The base-exchangeable capacity of the clay must not be too low, for example, clays of low exchange capacity such as kaolins, cannot form hard crumbs.

(c) The exchangeable ions on the clay must not be too large, for example, large complex organic exchangeable cations inhibit crumb formation.

(d) The paste from which the crumbs are made must be dispersed in a polar liquid.

(e) The polar molecules of the dispersion liquid must not be too large.

If water instability of crumbs is caused by the large resultant negative charges built up on neighboring clay particles, the lowering of the zeta potential of the colloidal system will reduce the force of repulsion between neighboring clay particles.

Baver (5) suggested that the irreversibility of colloidal iron hydroxide is the important factor in the production of stable aggregates in lateritic soils. A study of the bentonite floccules formed by  $\text{Fe}^{+++}$  and  $\text{Al}^{+++}$  and stabilized by drying, showed that the crystal plates were oriented in the horizontal plane and appeared to be covered with some material which existed homogeneously throughout the aggregates. This material was interpreted as being hydrous Fe and Al oxides acting as binding agents (25).

Weldon et al. (56) studied some samples from the Agronomy Farm at Kansas State University and found that the amount of sesquioxides extracted from the well aggregated fractions was considerably greater than that extracted from the poorly aggregated fractions, and concluded that in the prairie soils, sesquioxides acting as a cementing agent should not be overlooked. Chesters et al. (10) studied the relative importance of diverse factors affecting aggregation in 4 Wisconsin soil types by multiple regression analyses. Single and combined effects of pH and contents of organic matter, microbial gum,



clay and free iron oxide were considered. They found that in the Kawaunee soil, which has a relatively high content of clay and iron oxide, the iron oxide was of prime importance. They formulated the following algebraic expression to explain the amount of aggregation:

$$\begin{aligned} \% \text{ aggregation} = & 2.6 \times \% \text{ OM} + 326 \times \% \text{ microbial gum,} \\ & + 0.57 \times \% \text{ clay} + 11.8 \times \% \text{ free iron} \\ & \text{oxide} + 0.1 \times \text{pH} + 6.1 \end{aligned}$$

Peterson (43) showed that hydrous ferric oxide gel added to kaolinite did not increase the slight amount of water-stable structure which had developed in previously puddled pellets of that clay mineral and sand under the influence of cyclic wetting and drying. Little effect was noticed in the montmorillonite and sand until the amount of ferric oxide gel was equal to 1.5% of the dry weight of the sand and clay. He attributed the globular mass formation to the mutual coagulation of the negative montmorillonite gel by the positive ferric oxide gel. Sumner (50) showed that the charge of  $\text{Fe}_2\text{O}_3$  is positive at low, and negative at high pH values, accounting for a considerable portion of the pH dependent negative charge in soils. A considerable fraction of the surface of the clay fraction is covered by  $\text{Fe}_2\text{O}_3$ , resulting in decreased negative charge on the clay.

The following interactions between iron oxide and kaolinite may take place at crystal edges (Fig. 7) (12).



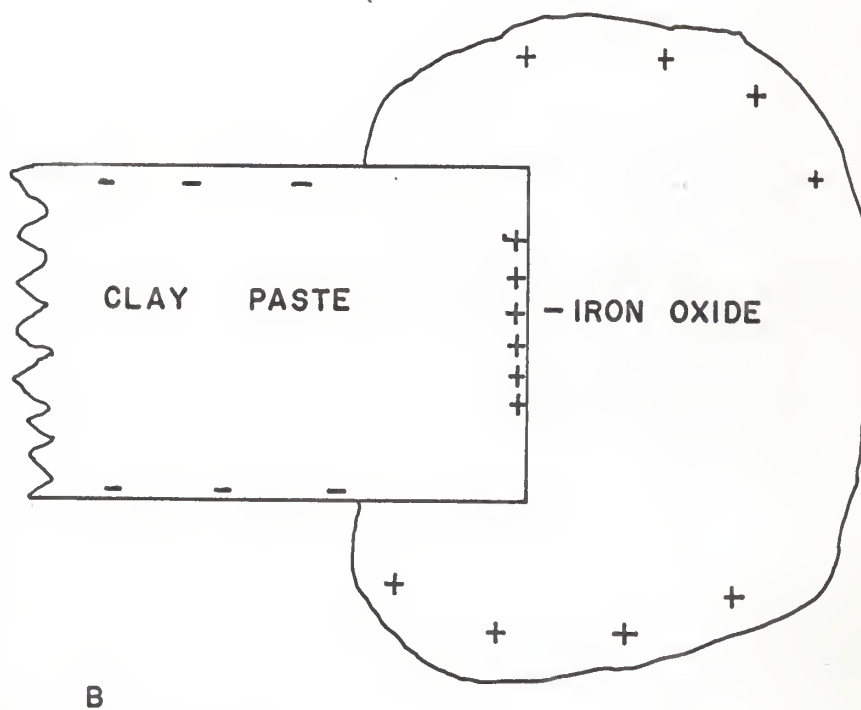
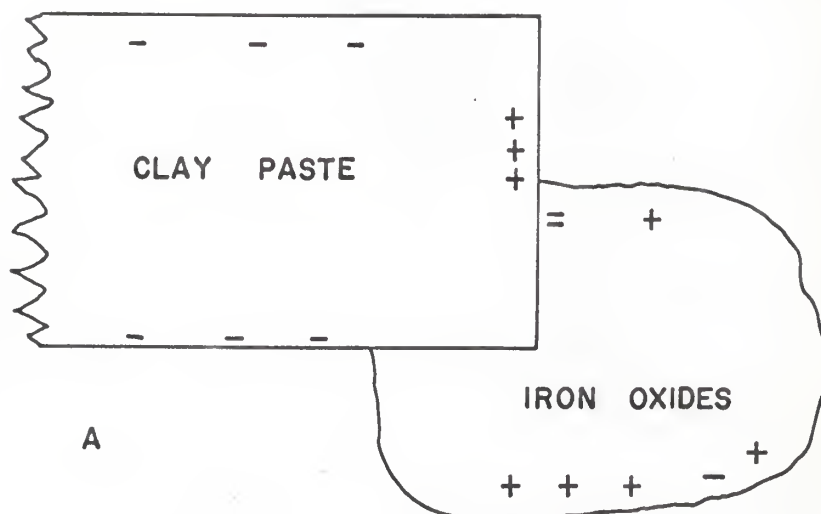


Fig. 7. The blocking of negative charges on Kaolinite by iron oxides.

(a) Positive charges associated with iron oxides may neutralize the negative charges on the clay;

(b) Edge hydroxyls of the clay and those from hydrated iron oxides may condense as water during dehydration; and

(c) Edge charges may be blanketed physically by iron oxides.

There is evidence to show that iron oxides have a surface charge density varying from  $0.5$  to  $1 \times 10^{-7}$  me/cm<sup>2</sup>. While that for the edges of kaolinite is about  $5 \times 10^{-7}$  me/cm<sup>2</sup>. Because of this disparity, it is therefore likely that neutralization of edge charges can take place only to a limited degree, but a large number of such charges could be physically covered as illustrated in (b), (a) is the hypothetical case and the assumption that charges at the clay-iron oxide interface naturally neutralize each other.

Since the degree of aggregation is a measure of structural properties of soils, Lutz (31) classified the cementing materials into three groups as follows:

(a) Organic colloidal material.

(b) Inorganic irreversible or slowly reversible colloids.

(c) Cohesive forces between colloidal clay particles.

He stated that the aggregation of lateritic soils is caused by the inorganic irreversible or slowly reversible colloids.

The data he obtained (Table 9) and the graph (Fig. 8) derived from these show a high correlation between the free iron content and the degree of aggregation of the silt and clay.

McIntyre (39) derived a plot of macroporosity (air space at 100 cm water tension) against the percentage of ferric oxide in the

Table 9. The relation of free iron oxide to the aggregation of silt and clay.

Soil type and horizon	Per cent free $\text{Fe}_2\text{O}_3$	Per cent silt and clay aggregated
Alamance silt loam A	0.524	25.6
Georgeville Clay A	3.975	72.4
" " B	4.313	55.0
Iredell sandy clay loam A	4.090	66.0
" " " " B	4.820	74.0
Cecil fine sandy loam A	4.736	28.2*
" " " " B	5.020	72.0
Davidson clay A	5.059	83.0
" " B	5.331	92.0
Davidson clay No. 2B	5.476	83.3

\*The Cecil A horizon contained only 18% clay and 11% silt. Aggregation of silt and clay is usually not very great in soils with such a high percentage of sand.

clay ( $< 2\mu$ ), this being considered more important than the free ferric oxide associated with total soil as far as structure is concerned.

The complete plot of these soils showed an increase in macroporosity with the free  $\text{Fe}_2\text{O}_3$  content of the clay as shown in Fig. 9. A regression of macroporosity on free  $\text{Fe}_2\text{O}_3$  gave a regression coefficient which is highly significant ( $P < 0.001$ ). The significance was based on the assumption that the value of free  $\text{Fe}_2\text{O}_3$  obtained in chemical analysis was that of the sample taken for physical measurements. That a regression of such high significance could be obtained on free  $\text{Fe}_2\text{O}_3$  without considering organic matter would indicate that in these soils the main influence on the structure was iron acting

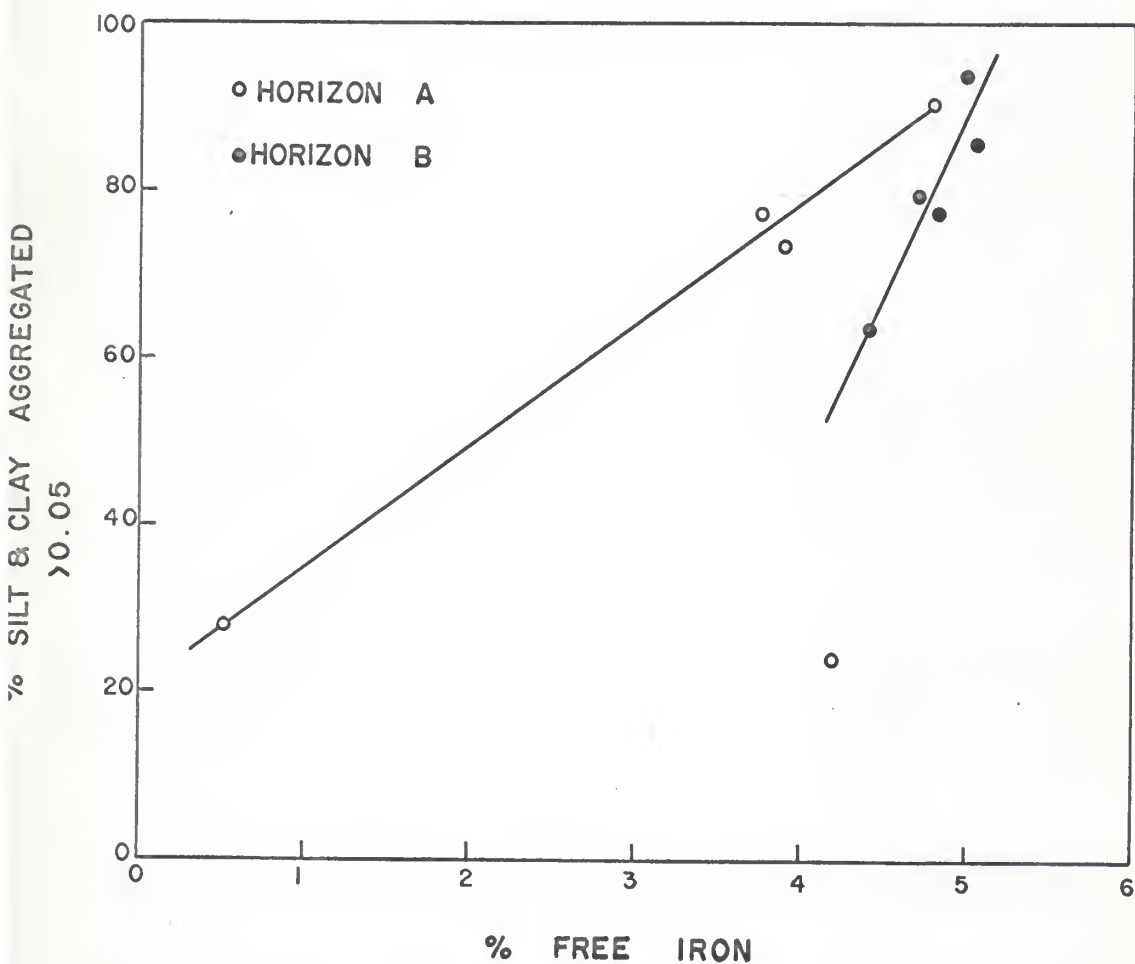


Fig. 8. The relation of free iron to the aggregation of silt and clay.



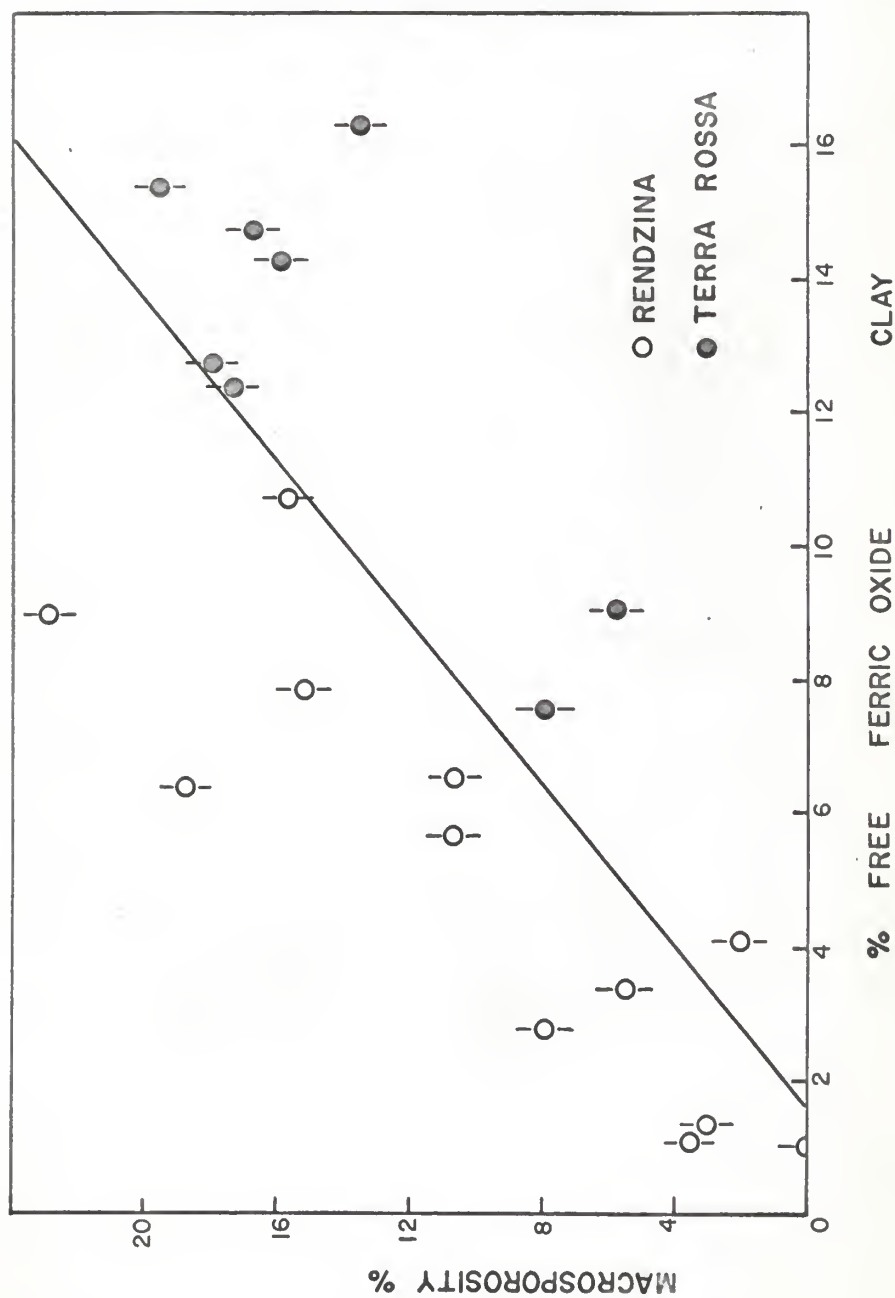


Fig. 9. Relation between macrospores of the soil and free ferric oxide in the clay fraction.

through the medium of an iron-organic matter complex. McIntyre postulated that the role of free iron in aggregation could be ascribed to one or all of the following:

(a) Cementation due to precipitation of hydrated iron gel and its irreversible dehydration.

(b) Iron in solution preventing deflocculation.

(c) The formation of organo-mineral compounds of humic acids with free sesquioxides.

A controversial point was introduced in 1964 by Deshpande et al. (14), when these research workers challenged the claim that iron oxide cemented the soil particles. They pointed out that the widespread belief that iron oxides were important aggregation of soil had arisen because:

(a) None of the currently used methods for the removal of iron oxides is specific as they also remove appreciable amounts of aluminum oxides and organic matter, and suitable controls have not been used to distinguish the effects of the different materials removed.

(b) The large amounts of iron oxides in many lateritic soils suggest obvious correlations with their physical properties. They thought that aluminum was responsible since it is well known that Al oxide forms interlayers with clay minerals, thus should not be surprising that it should bond clay particles together. Ferric oxide does not form such interlayers, although chlorites containing high proportions of ferrous iron in the brucite layer are well known. This anomaly had been previously pointed out by Prebble et al. (44) who emphasized that aluminum could be just as effective as iron in this role.

## DISCUSSION

In considering soil crumb formation, flocculation was assumed to be essential, and in fact, the cause of a stable crumb structure. As pointed out by Russell (45) two separate problems were, however, muddled up in this assumption, namely, the mechanism by which soil particles can hold together to form aggregates when dry, and the reasons why these aggregates may or may not hold together on subsequent re-wetting. The process of flocculation is generally pictured as the separation of a dispersed phase, in the form of flocs, from a dispersion medium. This process is a sufficient, though not a necessary condition that the crumbs formed by drying the dispersion medium shall be water-stable. Colloidal material must be present in a soil for it to be able to form crumbs. Pure sands and silts for example, cannot form crumbs or aggregates. Flocculation can be brought about by reducing the zeta potential to a low value called the critical point, as shown in Fig. 10.

### Zeta Potential

When colloidal particles have a high charge or high potential, they repel each other just as all like charges repel one another. There is a close relation between the zeta potential of colloidal particles and the amount of electrolyte necessary to flocculate the system (21). Considering the Gouy diffuse layer concept of colloidal systems as shown in Fig. 10, zeta potential can be thought of as part of the potential contributed by ions in the movable layer. Factors

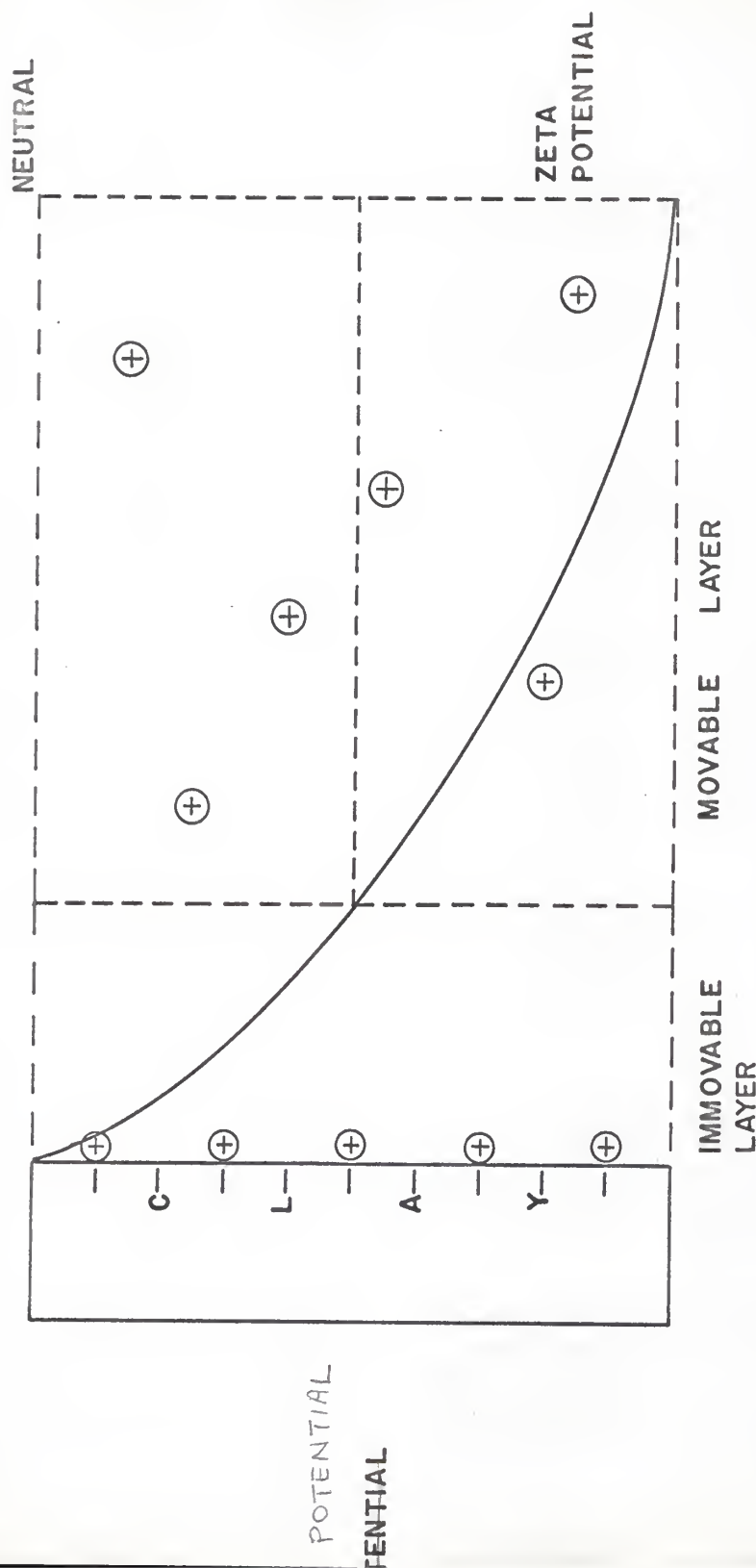


Fig. 10. Gouy diffuse layer concept of colloidal system.



influencing it are:

(1) Hydration of the clay. The more the hydration of the clay particle the greater the zeta potential. Kaolinite does not swell appreciably on wetting.

(2) Charge and size of the adsorbed cations. For rare gas type ions of equal size the zeta potentials of the clays tend to be lower as the electrical charge of the adsorbed ion is higher. The role of ionic size can be formulated as follows: "for rare gas-type ions of equal valency the zeta potential is the higher, the smaller the adsorbed cation." This observation is in agreement with Wegner's idea, according to which the most hydrated ion (small ions are very strongly hydrated) bring about the highest zeta potential.

(3) Valence of the adsorbed cation. The higher the valence of the cation adsorbed the more the neutralization of the negative charges on the colloid, and the lower the zeta potential.

(4) Addition of electrolytes. There is always an equilibrium between the movable and the immovable layers, thus when we add an electrolyte, we increase the positive charge in the movable layer and for equilibrium to be established, some positively charged ions have to transfer from the movable to immovable layer. The zeta potential is thus reduced.

#### Zeta Potential in Relation to Flocculation Values

It takes much more electrolyte to flocculate a clay with a high potential than one with a low potential. The relation between the

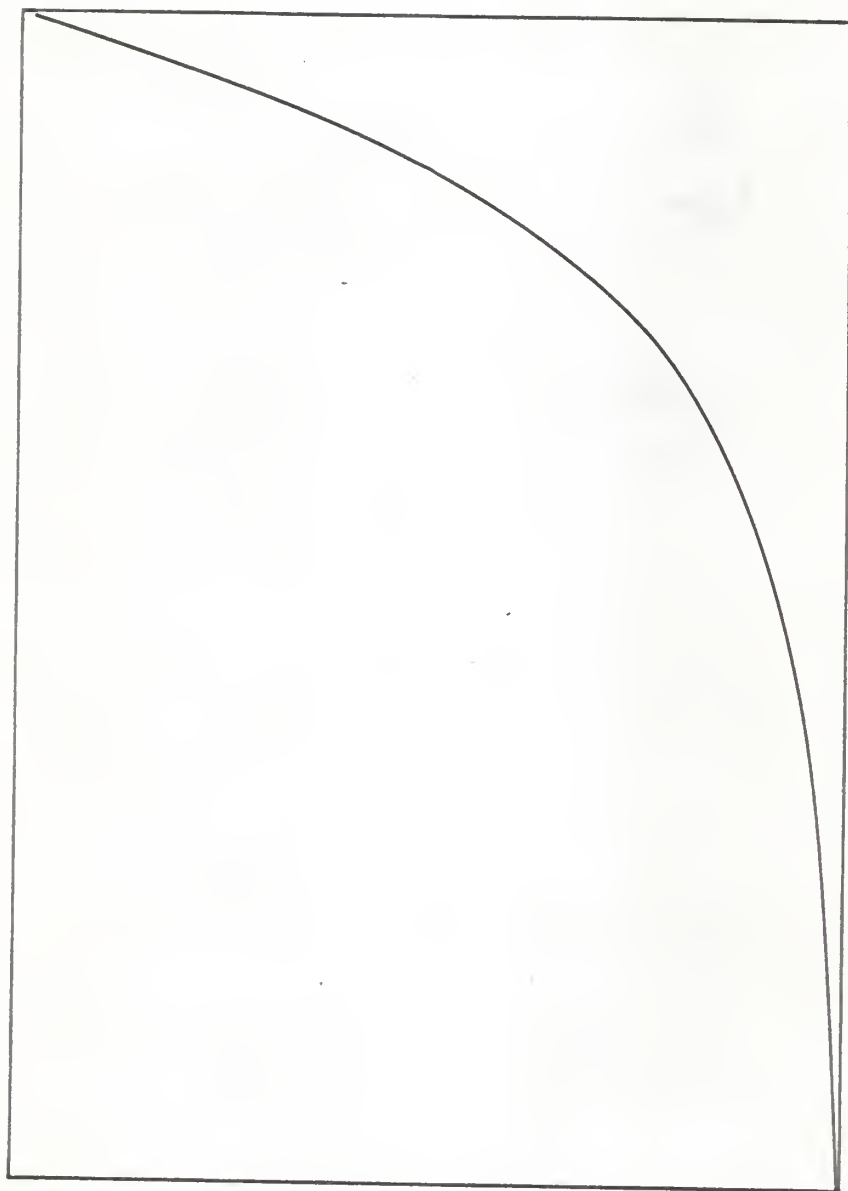
flocculation value and the zeta potential is a parabolic form, showing that the stability increases many-fold with a slight rise in zeta potential as shown in Fig. 11.

#### Flocculation Values and Exchange Adsorption

Two important cases must be separated. First, the cation of the electrolyte and colloidal particles possessing common ion only (eq. K-clay and KCl), secondly the coagulation agents contain only foreign ions with respect to the particle. In the former case flocculation results from repression of the double layer. In the second case it constitutes a combination of ionic exchange and the repression phenomenon. A comparison of flocculation values and ionic exchange data points towards an intimate association of the two phenomena. For any specific clay system those ions which are poorly adsorbed yield high flocculation values, while cations easily taken on by the colloidal particle coagulate the system at relatively low electrolyte concentration.

#### Mechanism of Soil Colloids Coagulation

Flocculation can be brought about by reducing the zeta potential to a low value called the critical potential, this is usually brought about by the addition of an electrolyte or an electrolyte and a dehydrating agent to the system. The electrolyte causes a repression of the outer layer of the double layer with a corresponding decrease in the zeta potential until flocculation occurs, as shown in Fig. 12.



FLOCCULATION  
VALUE

ZETA POTENTIAL

Fig. 11. Zeta potential in relation to flocculation value.

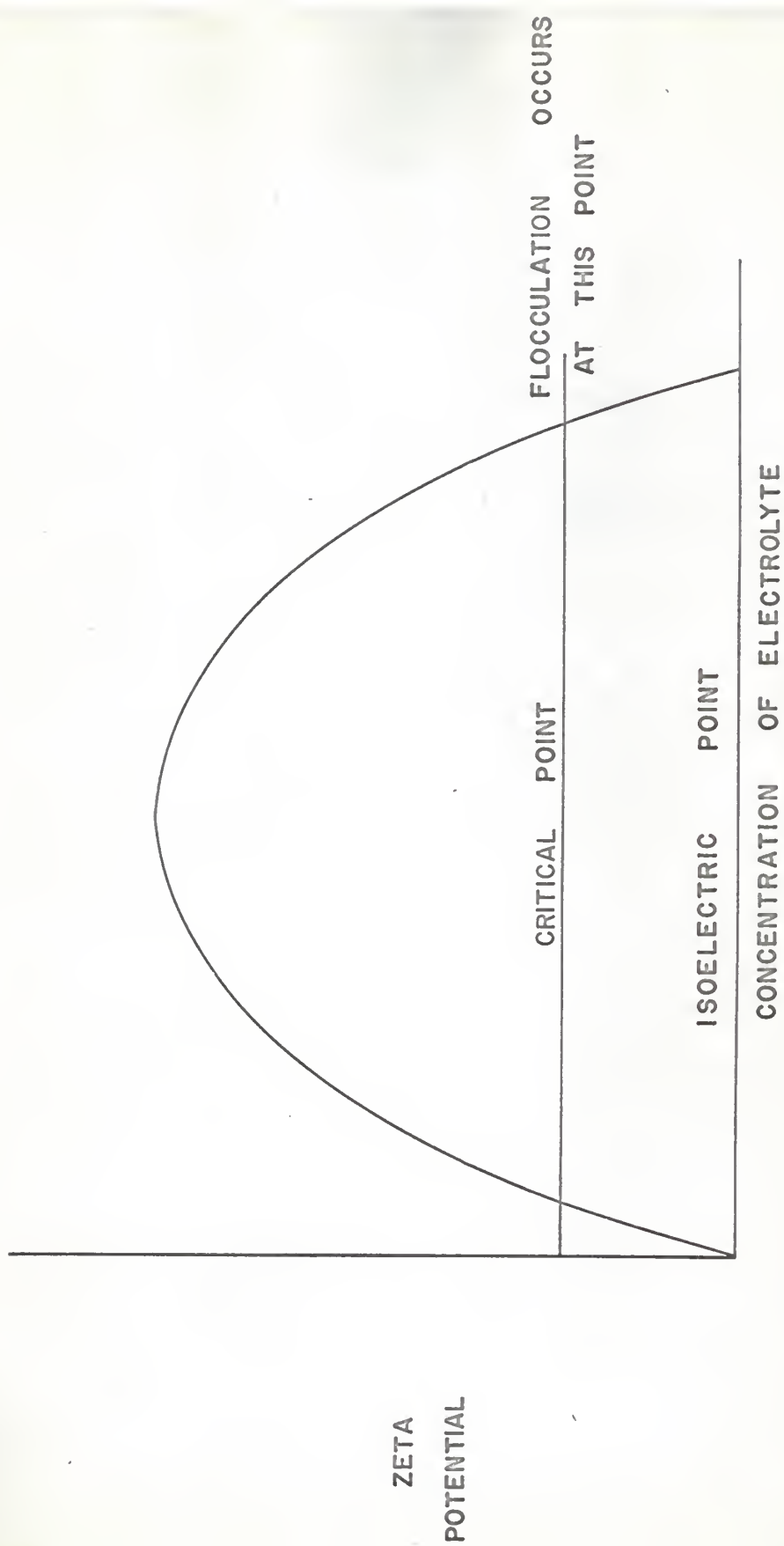


Fig. 12. Relationship between zeta potential and concentration of electrolyte added.



Considering a colloidal system, Fig. 13(a), on adding an electrolyte such as  $K_2SO_4$  to the sol the divalent  $SO_4^{=}$  being more strongly adsorbed than  $Cl^-$  forces itself into the double layer closer to the adsorbed  $H^+$  and  $Fe^{+++}$  ions and displaces  $Cl^-$  as indicated in Fig. 13(b). The adsorbed  $SO_4^{=}$  lowers the potential on the particle in the following way (53). The adsorbed  $SO_4^{=}$  ion has the same average kinetic energy as a  $Cl^-$  ion but it possesses double the charge. Accordingly if one assumes for the moment that the valence only determines the adsorbing power the divalent particles in the outer layer would be drawn close to the inner layer and the thickness of the double layer would be decreased. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it follows that the reduced thickness of the layer will be accompanied by a decrease in potential on the particle. Bradfield (7) showed that the coagulation value of colloidal clay may vary widely with slight changes in either of the following:

- (a) hydrogen ion concentration
- (b) concentration of the soil clay or
- (c) in the nature and extent of the exchange reactions which take place when a coagulating agent is mixed with the clay.

Bruton et al. (9) considering the coagulative power of any given ion postulated that it varies with concentration of the dispersed phase of the colloidal solution according to the following laws:

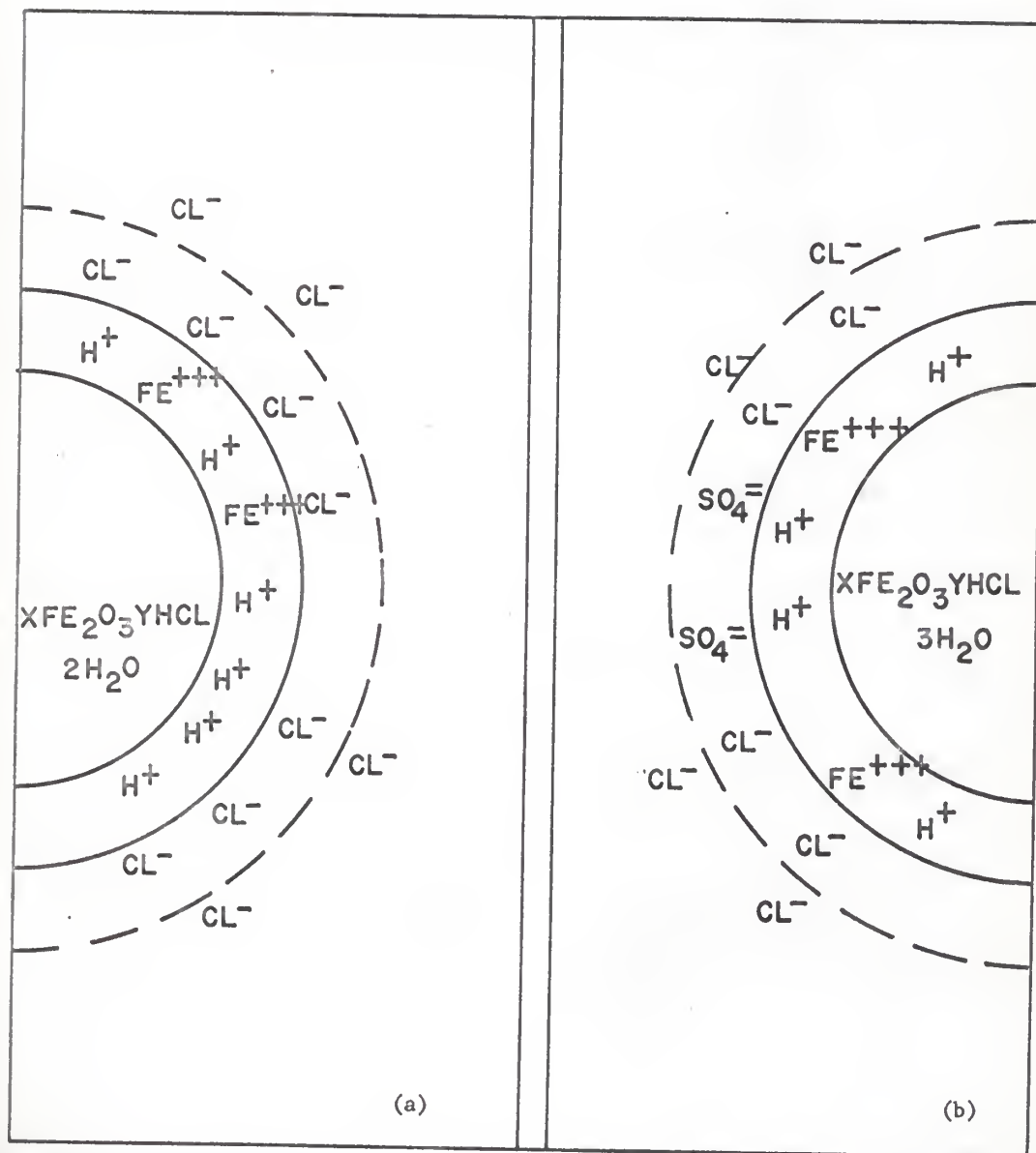


Fig. 13. The comparison of (a) chloride ions and (b) sulphate ions added to a colloidal system.

(a) For univalent ions the concentration of the ion necessary to produce coagulation increased with decreasing concentration of the colloid--this increase being very rapid with low concentrations of the colloid.

(b) For divalent ions the concentration of ion necessary to produce coagulation is almost constant and independent of the concentration of the colloid.

(c) For trivalent ions the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

#### The Mechanism of the Mutual Coagulation Process

The zone of complete mutual coagulation of two sols of opposite sign may be very narrow or quite broad (54, 55). The presence of free electrolytes in the oppositely charged sols has a marked effect on the width of the zone of mutual coagulation and the composition of the coagulum. The zone of mutual coagulation is quite narrow if the intermicellar solutions in both sols contain little or no free electrolytes or if the free electrolyte which is present contains ions of low precipitating power. In such a case the electrical neutralization by mutual adsorption of oppositely charged colloidal particles is the prime factor in determining the mutual coagulation. The zone of mutual coagulation is broad if one of the sols, say the negatively charged sol contains an electrolyte with an anion of high precipitating power. In this case the precipitating anion in the

intermicellar solution exerts a coagulating action on the positive sol that is independent of, but supplements the coagulation by mutual adsorption of oppositely charged particles. The precipitating power of positive sols for negative sol is not determined exclusively by the charge on the colloidal particles. Other factors which influence the mutual coagulation process are:

- (a) Mutual adsorption of colloidal particle, that is independent of their charge.
- (b) The presence of precipitating ions as impurities in the sols.
- (c) Interaction between stabilizing ions.

#### Coagulation of Lateritic Soils

Since lateritic soils have kaolinite as the predominating clay mineral, and since part of the negative charges on kaolinite are blocked by hydrated iron oxide, only a small amount of  $\text{Fe}^{+++}$  in solution will be necessary to flocculate the kaolinite colloid. This was shown by Lutz (30) who reported that only a small amount of iron flocculated the Davidson soils. Joffe (22) pointed out that Aarniol showed that  $\text{SiO}_2$  and humus colloids precipitate Fe and Al, the former being precipitated to a greater extent. He also added that Udulft in his experiments with the sols of Fe, Mn, clay, and humus showed that the movement of the Fe sol was helped by the protective action of the Mn sol, but was flocculated by the carbonate ion and by humus. The latter by mutual coagulation of colloids,  $\text{Fe}_2\text{O}_3$  sol is positively charged at low pH values and humus sol is always negatively charged.



In the study of the mutual coagulation and peptization of iron oxide and humus sols, it was found that the amount of humus necessary for the full peptization of a sol containing 100 parts of iron oxide per million of solution with a pH value around 4.0 was not more than about 1/3 the amount of iron oxide (13).

#### SUMMARY

The role of free iron in aggregation is not fully understood. The aggregating influence has been ascribed to one or all of the following:

- (a) Cementation due to precipitation of a hydrated iron gel and its irreversible hydration.
- (b) Iron in solution preventing deflocculation.
- (c) The formation of organo-mineral compounds of humic acids with free sesquioxides.

The challenge by the Australian research workers casts a shadow of doubt on these claims. They maintain that aluminum is the prime factor in the aggregation of lateritic soils. Therefore, more work needs to be done to clarify the situation. The formation of soil concretions by free iron in lateritic soils is quite consistent with the already existing theory of anion adsorption by the hydrous ferric oxide. While free iron and organic matter can interact to form new complexes, if they are both free from exchangeable bases, there is not enough evidence that these new complexes play any special role in

aggregate formation, except that the range of molar complexes varying from 1:1 to 6:1 become increasingly more water-insoluble as more metal is complexed.

## LITERATURE CITED

1. Anderson, M. S. (1929). The influence of substituted cations on the properties of soil colloids. *J. Agr. Research* 38:565-584.
2. Anderson, M. S., and H. G. Byers. (1931). Character of the colloidal materials in the profiles of certain major soil groups. *U.S.D.A. Tech. Bull.* 228.
3. Anderson, M. S., and S. Mattson. (1926). Properties of the colloidal soil materials. *U.S.D.A. Bull.* 1452.
4. Barlett, R. J. (1961). Iron oxidation proximate to plant roots. *Soil Sci.* 92:372-379.
5. Baver, L. D. *Soil Physics*, 3rd Edition. John Wiley & Sons, Inc., New York.
6. Bear, F. E., and S. Toth. (1942). Phosphate fixation in soils and its practical control. *J. Ind. Eng. Chem. (Ind. Ed.)* 34:49-52.
7. Bradfield, R. (1928). Factors affecting the coagulation of colloidal clay. *J. Phys. Chem.* 32:202-208.
8. Bromfield, S. M. (1965). Studies of the relative importance of iron and aluminum in the sorption of phosphate by Australian soils. *Australian Jour. of Soil Res.*, 3:31-44.
9. Burton, E. F., and Miss E. Bishop. (1920). Coagulation of colloidal solutions by electrolytes. Influence of concentration of sol. *J. Phy. Chem.* 24:701-715.
10. Chesters, G., O. J. Attoe and O. N. Allen. (1957). Soil aggregation in relation to various soil constituents. *Soil Sci. Soc. Amer. Proc.* 21:272-277.
11. Clark, J. S. (1964). Al and Fe fixation in relation to exchangeable hydrogen in soils. *Soil Sci.* 98:302-306.
12. Davidtz, J. C., and M. E. Sumner. (1965). Blocked charges on clay minerals in sub-tropical soils. *J. Soil Sci.* 16:270-274.
13. De d , B. C. (1949). The movement and precipitation of iron oxides in podzol soils. *J. Soil Sci.* 1:113-122.
14. Deshpande, T. L., D. J. Greenland, and J. P. Quirk. (1964). The role of iron oxides in the bonding of soil particles. *Nature London* 201:107-108.

15. Ensminger, L. (1954). Some factors affecting the adsorption of sulphate by Alabama soils. *Soil Sci. Soc. Amer. Proc.* 18: 259-264.
16. Hardy, F., and G. Rodrigues. (1939). Soil genesis from andesite in Grenada British West Indies. *Soil Sci.* 48:361-384.
17. Hemwall, J. B. (1957). The fixation of phosphorus in soil. *Adv. in Agron.* 9:95-112.
18. Hsu Pa Ho. (1964). Adsorption of phosphate by aluminum and iron in soils. *Soil Sci. Soc. Amer. Proc.* 28:474-478.
19. Hsu Pa Ho and D. A. Rennie. (1962). Adsorption of phosphate by X-ray amorphous aluminum hydroxides. *Cand. J. Soil Sci.* 42:197-209.
20. Ignatieff, V. (1939). Ferrous iron in soils. *Nature* 143:562-563.
21. Jenny, H., and R. F. Reitemeier. (1935). Ion exchange in relation to the stability of colloidal systems. *J. Phy. Chem.* 39:593-604.
22. Joffe, J. S. (1930). Experiments on the movement of iron and aluminum in the soil. 2nd Inter. Congress of Soil Sci. 2: 135-145.
23. Joffe, J. S., and H. C. McLean. (1928). Colloidal behaviour of soils and soil fertility. V. The distribution of soluble and colloidal iron and aluminum in soils. *Soil Sci.* 26: 317- 25.
24. Kamprath, E. J., W. L. Nelson, and J. W. Fitts. (1956). The effect of pH, sulphate and phosphate concentrations on the adsorption of sulphates by soils. *Soil Sci. Soc. Amer. Proc.* 20:463-466.
25. Kroth, E. M., and J. B. Page. (1946). Aggregate formation in soils with special reference to cementing substances. *Soil Sci. Soc. Amer. Proc.* 11:27-34.
26. Kubiena, W. (1962). Taxonomic importance of the type and formation of iron oxide minerals in tropical soils. *Soils and Fertilizers.* Vol. XXV:467.
27. Larsen, B., D. Gunary and C. D. Sutton. (1965). The rate of immobilization of applied phosphate in relation to soil properties. *J. Soil Sci.* 16:141-148.



28. Lichtenwalner, D. C., A. L. Flenner, and N. E. Gordon. (1923). Adsorption and replacement of plant food in colloidal oxides of iron and aluminum. *Soil Sci.* 15:157-165.
29. Low, P. F., and C. A. Black. (1948). Phosphate induced decomposition of kaolinite. *Soil Sci. Soc. Amer. Proc.* 12:180-184.
30. Lutz, J. F. (1934). The physico-chemical properties of soils affecting soil erosion. *Missouri Agric. Expt. Station Res. Bull.* 212.
31. Lutz, J. F. (1936). The relation of free iron in the soil to aggregation. *Soil Sci. Soc. Amer. Proc.* 1:43-45.
32. Lutz, J. F. (1938). The effect of iron on some physico-chemical properties of Bentonite suspensions. *Soil Sci. Soc. Amer. Proc.* 3:7-12.
33. Martin, F. J., and M. A. Doyne. (1927). Laterite and lateritic soils in Sierra Leone. *J. Agric. Sci.* 17:530-547, 20(1930): 135-143.
34. Mattson, S. (1926). Electrokinetic behavior and base exchange. *Jour. Amer. Soc. Agron.* 18:458-470.
35. Mattson, S. (1927). Anion and cationic adsorption by soil colloidal materials of varying  $\text{SiO}_2/\text{Al}_2\text{O}_3$   $\text{Fe}_2\text{O}_3$  ratio. *Intern. Congress of Soil Sci. Proc.* V2:199-211.
36. Mattson, S. (1928). The action of neutral salts on acid soils with reference to aluminum and iron. *Soil Sci.* 25:345-350.
37. Mattson, S. (1930). The laws of soil colloidal behavior: III isoelectric precipitates. *Soil Sci.* 30:459-495.
38. Maud, R. R. (1965). Laterite and lateritic soil in coastal Natal, South Africa. *J. Soil Sci.* 16:60-72.
39. McIntyre, D. S. (1956). The effect of free ferric oxide on the structure of some Terra Rosa and Rendzina soils. *J. Soil Sci.* 7:302-306.
40. Oades, J. M. (1963). The nature and distribution of iron compounds in soils. *Soils and Fertilizers XXVI*:69-80.
41. Olson, R. V. (1947). Iron solubility in soils as affected by pH and free iron oxide content. *Soil Sci. Soc. Amer. Proc.* 12:153-157.
42. Paver, H., and C. E. Marshall. (1934). The role of aluminum in the reactions of the clay. *Chem. and Industry*, 53:750-760.

43. Peterson, J. B. (1946). The role of clay minerals in the formation of soil structures. *Soil Sci.* 61:247-256.
44. Prebble, R. E., and G. B. Stirk. (1959). The effect of free iron oxide on range of available water in soils. *Soil Sci.* 88:213-217.
45. Russell, E. W. (1938). Soil structure. *Imp. Bureau of Soil Sci. Tech. Bull.* No. 37.
46. Schnitzer, M., and S. I. M. Skinner. (1963). Organo-metallic interactions in soils. I. Reactions between a number of metal ions and the organic matter of a podzol B<sub>h</sub> horizon. *Soil Sci.* 96:86-96.
47. Schnitzer, M., and S. I. M. Skinner. (1963). Organo-metallic interactions in soils. II. Reactions between different forms of iron and aluminum and the organic matter of a podzol B<sub>h</sub> horizon. *Soil Sci.* 96:181-186.
48. Schnitzer, M., and S. I. M. Skinner. (1964). Organo-metallic interaction in soils. III. Properties of iron and aluminum organic matter complexes prepared in the laboratory and extracted from a soil. *Soil Sci.* 97:197-203.
49. Schnitzer, M., and S. I. M. Skinner. (1965). Organo-metallic interactions in soils. IV. Carboxyl and hydroxyl groups in organic matter and metal retention. *Soil Sci.* 99:278-284.
50. Sumner, M. E. (1964). Effect of iron oxides on positive and negative charges in clays and soils. *Soils and Fertilizers.* V. XXVII:120.
51. Toth, S. J. (1937). Anion adsorption by soil colloids in relation to charges in free iron oxides. *Soil Sci.* 44:299-314.
52. Wadsworth, H. A. (1935). A note on the relationship between the chemical compositions of soil colloids and two of their properties. *Soil Sci.* 39:171-176.
53. Weiser, H. B. Inorganic colloid chemistry. V. 2. The hydrous oxides and hydroxides. John Wiley and Sons, Inc. N. Y.
54. Weiser, H. B., and T. S. Chapman. (1931). The mechanism of the mutual coagulation process I. *J. Phys. Chem.* 35:543-556.
55. Weiser, H. B., and T. S. Chapman. (1932). The mechanism of the mutual coagulation process. II. *J. Phys. Chem.* 36:713-721.
56. Weldon, T. L., and J. C. Hide. (1942). Some chemical properties of soil organic matter and of sesquioxides associated with aggregation in soils. *Soil Sci.* 54:343-355.

**THE ROLE OF IRON COMPOUNDS ON THE STRUCTURE  
OF LATERITIC SOILS**

by

**WILSON BAMIKOLE IPINMIDUN**

**B.Sc. (Special), London University, 1963**

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**AN ABSTRACT OF A MASTER'S REPORT**

**submitted in partial fulfillment of the**

**requirements for the degree**

**MASTER OF SCIENCE**

**Department of Agronomy**

**KANSAS STATE UNIVERSITY  
Manhattan, Kansas**

**1966**



The purpose of this report was to collect and discuss information obtained in various parts of the world concerning the role of iron compounds on the structure of lateritic soils.

Lateritic soils occur mostly in the tropics. Kaolinite is the predominant clay mineral in these leached soils and they contain a considerable amount of hydrous oxides of iron and aluminum. They are not plastic, do not swell on wetting, are permeable, have a low base exchange capacity, have silica: alumina ratios between 1.33 and 2.0, and are easy to cultivate when wet.

It was suggested that the role of free iron oxide, the most abundant form of free iron in these soils, could be ascribed to one or all of the following:

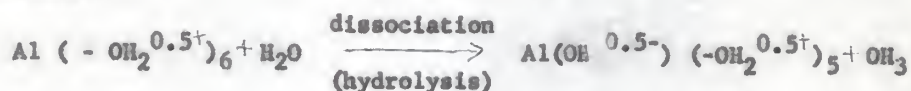
- (a) Cementation due to precipitation of hydrated iron gel and its irreversible hydration.
- (b) Iron in solution preventing flocculation.
- (c) The formation of organo-mineral compounds of humic acid with free sesquioxides.

Since some of the negative charges associated with kaolinite clay are blocked by the positively charged hydrous ferric oxide, only a small amount of iron is necessary for the coagulation of the kaolinite clay colloid. The mutual coagulation of hydrous iron oxide and humus sols is brought about, because hydrous ferric oxide sol is positively charged at low pH values and humus is always negative. There are indications of the formation of a range of molar complexes between ferric iron, aluminum and organic matter. The ratios of metal to organic matter varying from 1:1 to 6:1, involving in each instance



one COOH group per atom of metal. These molar complexes become increasingly water-insoluble as more metal is complexed. This suggested predominant role of free iron oxide on the structure of lateritic soils was challenged in 1964, when some Australian research workers thought that the emphasis should be placed on aluminum oxide instead of iron oxide, since aluminum oxide could take part in all the roles ascribed to ferric oxide and in addition could form interlayers with clay minerals.

Both polyvalent anions (such as sulphate) anionic colloidal electrolytes (such as expansible layer silicates) exert polarization and steric pinching effects which increase the aluminohydronium polymerization rate by decreasing the distance between hydroxy-nonomers and polymers, normally formed by the dissociation reaction formed as follows:



This results in the expulsion of  $\text{OH}_3^+$  into the solution. The aluminohydronium functional groups are located at the structural edges of the polymeric interlayers and at silicate layer edges as well as attached to organic cation exchange sites. They can also be considered as part of the cation exchange mechanism, Al-O sharing in the retention of exchangeable H more or less suspended between the layers and interlayer structures.

Since the role of iron compounds has not been fully established, and since the suggested role of iron oxide has been challenged, more work needs to be done on this problem to clarify the situation.